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PATENT APPLICATION

MULTIFUNCTIONAL ANTIMICROBIAL DYES

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MULTIFUNCTIONAL ANTIMICROBIAL DYES

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 60/456,620, filed March 19, 2003, which is herein incorporated by reference in its entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with Government support under Grant No. DMI 9733981 awarded by the National Science Foundation. The Government has certain rights in this invention.

FIELD OF THE INVENTION

[0003] The present invention relates to novel antimicrobial cationic dyes and methods for using the same. In particular, the antimicrobial cationic dyes of the present invention are useful for the simultaneous dyeing and functional finishing of polymers, *e.g.*, textiles.

BACKGROUND OF THE INVENTION

[0004] Textile dyeing and functional finishing are two necessary but traditionally separated processes employed in textile treatments. Textile dyeing and finishing necessitate repeated wet treatments and drying, and thus consume large quantities of energy and produce large amounts of wastewater. Simultaneous dyeing and finishing of textiles in one bath provides both economical and environmental advantages in textile manufacturing. Recent studies have demonstrated that the combination of these two processes is feasible (Lewis *et al.*, *J. Soc. Dyer Colorist*; 113:159 (1997); Choi *et al.*, *J. Appl. Polym. Sci.*; 54:2107 (1994); Kim *et al.*, *Textile Res. J.*; 70(8):728 (2000); Kim *et al.*, *Textile Res. J.;* 71(4):318 (2001)). However, such combinations are typically based on the simple mixing of dyes, finishes, and other auxiliaries, compromising dyeing and/or finishing conditions and sacrificing the properties of the resultant textiles.

[0005] Generally speaking, dyes and colorants are compounds whose electronic structures can absorb electromagnetic radiation in the visible range (380-780 nm). Additional

properties other than color can be defined as functions. Based on this definition, infrared dyes, laser dyes, and voltage sensitive dyes fall within the category of functional dyes (Griffiths J., *Chimia*; 45:304 (1991)). However, our concept of a functional dye is more specifically associated with the traditional functions that textile fabrics or clothing materials should possess. These functions can include, for example, antimicrobial, anti-static, softening, water-repellent, fire-resistant, soil-repellent, anti-UV, and anti-chemical properties.

[0006] Acrylic fabrics are widely used synthetic fabrics due to a combination of desirable properties, such as a soft, wool-like feel, good elasticity and mechanical properties, and high resistance to outdoor exposure and to many chemical compounds (Burkinshaw, *Chemical principles of synthetic fibre dyeing*, Glasgow: Blackie Academic & Professional, Chapman & Hall (1995)). Although extensive studies have been carried out in the cationic dyeing of acrylic fabrics (Bird *et al.*, *The theory of coloration of textiles*, London: Dyers Company Publications Trust (1975); Munn, *The dyeing of synthetic-polymer and acetate fibres*, England: Dyers Company Publications Trust (1979)), little is known about the functional finishing of acrylic fabrics. Recently, some progress has been made to introduce antimicrobial functions into acrylic fabrics either by N-halamine moieties or by quaternary ammonium salts (QAS) (Sun *et al.*, *Appl. Polym. Sci.*, 84:1592 (2002); Kim *et al.*, *Textile Res. J.*, 72:1052 (2002)). Unfortunately, both of these treatments limit and/or affect the dyeing of the finished acrylics because chlorine bleach is needed in N-halamine treatments and the QAS can occupy available dye sites within the fabrics, thus interfering with the dyeing behaviors of the resultant fabrics.

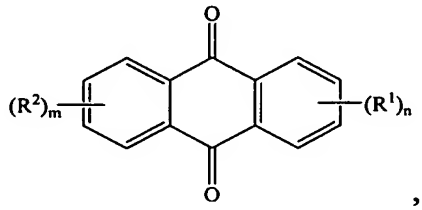
[0007] Thus, there is a need to unify textile dyeing and functional finishing into one process that: (1) does not compromise dyeing and/or finishing conditions; (2) does not sacrifice the properties of the resultant textiles; and (3) is more economical and environmentally friendly.

SUMMARY OF THE INVENTION

[0008] The present invention provides novel functional finishing dyes comprising at least one functional finishing group covalently attached to a traditional dye via a chemical linkage (*see,* Figure 1). More particularly, the present invention provides novel antimicrobial cationic dyes comprising a quaternary ammonium salt (QAS) group covalently attached to an aminoanthraquinioid dye via a linker. The dyes are particularly useful for imparting a functional property to a polymer, such as an antimicrobial, anti-static, softening, water-

repellent, fire-resistant, soil-repellent, anti-UV, or anti-chemical property, and for simultaneously dyeing and finishing a polymer.

[0009] In one aspect, the present invention provides a compound having the formula:



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wherein:

each R^1 is an independently selected quaternary ammonium salt group;

each R^2 is independently selected from a quaternary ammonium salt group and a substituent group;

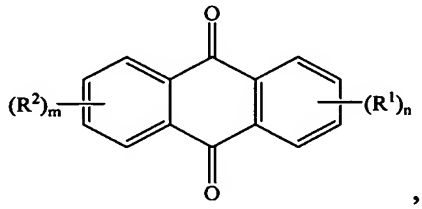
m is an integer from 0 to 4; and

n is an integer from 1 to 4.

[0010] In another aspect, the present invention provides a polymer composition comprising:

(a) a polymer, wherein the polymer is a member selected from the group consisting of a textile, a plastic, rubber, paint, a surface coating, an adhesive, and a combination thereof; and

(b) a compound having the formula:



I

wherein:

each R^1 is an independently selected quaternary ammonium salt group;

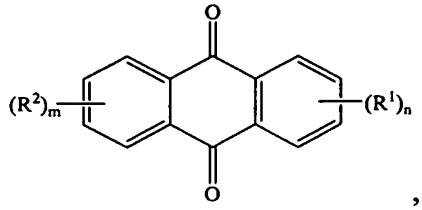
each R^2 is independently selected from a quaternary ammonium salt group and a substituent group;

m is an integer from 0 to 4; and

n is an integer from 1 to 4.

[0011] In yet another aspect, the present invention provides a method for simultaneously dyeing and finishing a polymer, the method comprising:

immersing the polymer in an aqueous treating solution which comprises a compound having the formula:



I

wherein:

each R^1 is an independently selected quaternary ammonium salt group;

each R^2 is independently selected from a quaternary ammonium salt group and a substituent group;

m is an integer from 0 to 4; and

n is an integer from 1 to 4.

[0012] There are a myriad of applications for the compounds, *i.e.*, the QAS-dyes, of the present invention. For example, polymers, *e.g.*, textile materials, can be treated with the QAS-dyes to provide a biocidal protective coating on the polymers effective against a variety of microorganisms. The treated polymers are suitable for use as clothing in the medical field as well as in related healthcare and hygiene areas. Treated polymers of the present invention can be fabricated into disposable or reusable textile materials.

[0013] The microbiocidal properties of the textiles of the present invention can be advantageously used for women's wear, underwear, socks, and other hygienic purposes such as upholsteries. In addition, the microbiocidal properties can be imparted to carpeting materials to create odor-free and/or germ-free carpets. Moreover, all germ-free environments, such as those required in biotechnology and the pharmaceutical industry, can benefit from the use of the microbiocidal textiles of the present invention to prevent any contamination from air, liquid, and/or solid media.

[0014] Other features, objects and advantages of the invention and its preferred embodiments will become apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Figure 1 illustrates the structure of a functional finishing dye of the present invention.

[0016] Figure 2A illustrates various structures of antimicrobial QAS-dyes of the present invention. Figure 2B illustrates preferred mono- and bi-QAS substituted dyes of the present invention.

[0017] Figure 3 illustrates a synthetic procedure for producing a dye of the present invention.

[0018] Figure 4 illustrates the ^{1}H NMR spectrum of the m-4 dye.

[0019] Figure 5 illustrates the ^{13}C NMR spectrum of the m-4 dye.

[0020] Figure 6 illustrates the FTIR spectra of representative mono-QAS substituted dyes.

[0021] Figure 7 illustrates the absorption spectra of a mono- and a bi-QAS substituted dye of the present invention in an aqueous solution.

[0022] Figure 8 illustrates the three types of hydrogen bonding in aqueous solutions: (a) intramolecular; (b) intermolecular; and (c) with water molecules.

[0023] Figure 9 illustrates the effect of dyeing time on an acrylic dyeing process (dye concentration: 1 mMol/L, pH: 3; bath ratio: 1:50; dyeing temperature: 100°C).

[0024] Figure 10 illustrates the effect of dye concentration on an acrylic dyeing process (pH: 3; bath ratio: 1:50; initial dyeing temperature: 95°C for 50 min.; fixation: 100°C for 10 min.).

[0025] Figure 11 illustrates the effect of initial dyeing temperatures on an acrylic dyeing process (dye concentration: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing: 50 min.; fixation: 100°C for 10 min.).

[0026] Figure 12 illustrates the FTIR spectra of (A) untreated Orlon; (B) Orlon dyed with m-4 (dye concentration: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing: 100°C for 50 min.; fixation: 100°C for 10 min.); (C) difference spectrum of B and A (*i.e.*, subtracting A from B); and (D) pure m-4.

[0027] Figure 13 illustrates the FTIR spectra of (A) untreated Orlon; (B) Orlon treated with bi-12 (dye concentration: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing:

100°C for 50 min.; fixation: 100°C for 10 min.), (C) difference spectrum of B and A (*i.e.*, subtracting A from B); and (D) pure bi-12.

[0028] Figure 14 illustrates the FTIR spectra of (A) untreated Orlon; (B) Orlon treated with m-4; (C) Orlon treated with m-8; (D) Orlon treated with m-12; (E) Orlon treated with bi-4; (F) Orlon treated with bi-8; and (G) Orlon treated with bi-12 (dye concentration: 1 mMol/L; pH: 3; bath ratio: 1:50; initial dyeing: 100°C for 50 min.; fixation: 100°C for 10 min.).

[0029] Figure 15 illustrates surface resistivity of an inventive Orlon fabric.

[0030] Figure 16 illustrates the DSC curves of a mono-QAS substituted dye.

[0031] Figure 17 illustrates the TGA curves of a mono-QAS substituted dye.

[0032] Figure 18 illustrates the UV-vis absorption spectra of m-4 at pH 5 and at 100°C (original dye concentration: 0.4 mMol/L).

[0033] Figure 19 illustrates the ^{1}H NMR spectrum of 1-amino anthraquinone (solvent: DMSO-d_6).

[0034] Figure 20 illustrates the ^{1}H NMR spectrum of carboxymethyl-butyl-dimethyl ammonium chloride (CBDAC).

[0035] Figure 21 illustrates the ^{13}C NMR spectrum of CBDAC.

[0036] Figure 22 illustrates the ^{1}H NMR spectrum of 1,4-diaminoanthraquinone.

[0037] Figure 23 illustrates the stability of a mono-QAS substituted dye at different pH and at 100°C (original dye concentrations: 1 mMol/L).

[0038] Figure 24 illustrates the stability of a bi-QAS substituted dye at different pH and at 100°C (original dye concentrations: 1 mMol/L).

DETAILED DESCRIPTION OF THE INVENTION

I. Definitions

[0039] "Alkyl" refers to a saturated linear monovalent hydrocarbon radical or a saturated branched monovalent hydrocarbon radical containing from 1 to 20 carbon atoms. Preferably, the alkyl radical contains from 1 to 4 carbon atoms (*i.e.*, C_1-C_4 alkyl) or from 4 to 18 carbons atoms (*i.e.*, C_4-C_{18} alkyl). Exemplary alkyl groups include, but are not limited to,

methyl, ethyl, *n*-propyl, 2-propyl, butyl, *iso*-butyl, *sec*-butyl, *tert*-butyl, pentyl, *iso*-amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like.

[0040] "Alkylene" refers to a saturated linear divalent hydrocarbon radical or a saturated branched divalent hydrocarbon radical containing from 1 to 20 carbon atoms. Preferably, the alkylene radical contains from 1 to 12 carbon atoms (*i.e.*, C_1-C_{12} alkylene). Exemplary alkylene groups include, but are not limited to, methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, and the like.

[0041] The term "cycloalkyl" refers to a cyclic alkyl radical containing from 3 to 8, preferably from 3 to 6, carbon atoms. Exemplary cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and the like.

[0042] The term "cycloalkylene " refers to a cyclic carbocycle radical containing from 4 to 8, preferably 5 or 6, carbon atoms and one or more double bonds. Exemplary cycloalkylene groups include, but are not limited to, cyclopentylene, cyclohexylene, cyclopentadienylene, and the like.

[0043] The term "aryl" refers to a carbocyclic aromatic radical selected from the group consisting of phenyl, naphthyl, indenyl, indanyl, azulenyl, fluorenyl, anthracenyl, and the like; or a heterocyclic aromatic radical selected from the group consisting of furyl, thienyl, pyridyl, pyrrolyl, oxazolyly, thiazolyl, imidazolyl, pyrazolyl, 2-pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, 1,2,3-oxadiazolyl, 1,2,3-triazolyl, 1,3,4-thiadiazolyl, pyridazinyl, pyrimidinyl, pyrazinyl, 1,3,5-triazinyl, 1,3,5-trithianyl, indolizinyl, indolyl, isoindolyl, 3H-indolyl, indolinyl, benzo [b]furanyl, 2,3-dihydrobenzofuranyl, benzo[b]thiophenyl, 1H-indazolyl, benzimidazolyl, benzthiazolyl, purinyl, 4H-quinolizinyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, 1,8-naphthyridinyl, pteridinyl, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, phenoxazinyl, and the like. The aryl group can also have from one to five substituents selected from the group consisting of hydrogen, halogen, hydroxyl, amino, nitro, trifluoromethyl, trifluoromethoxy, alkyl, alkylene, alkynyl, 1,2-dioxymethylene, 1,2-dioxyethylene, alkoxy, alkenoxy, alkynoxy, alkylamino, alkenylamino or alkynylamino, alkylcarbonyloxy, aliphatic or aromatic acyl, alkylcarbonylamino, alkoxycarbonylamino, alkylsulfonylamino, N-alkyl, N,N-dialkyl urea, and the like.

[0044] The term "alkoxyl" refers to an alkyl ether radical containing from 1 to 20 carbon atoms. Exemplary alkoxyl groups include, but are not limited to, methoxyl, ethoxyl, *n*-propoxyl, *iso*-propoxyl, *n*-butoxyl, *iso*-butoxyl, *sec*-butoxyl, *tert*-butoxyl, and the like.

[0045] The term "alkylamino" refers to a mono- or di-alkyl-substituted amino radical (*i.e.*, a radical having the formula: alkyl-NH- or $(alkyl)_2$-N-), wherein the term "alkyl" is as defined above. Exemplary alkylamino groups include, but are not limited to, methylamino, ethylamino, propylamino, *iso*-propylamino, *t*-butylamino, *N,N*-diethylamino, and the like.

[0046] The term "aralkyl" refers to an aryl radical, as defined herein, attached to an alkyl radical, as defined herein.

[0047] The term "cycloalkylalkyl" refers to a cycloalkyl radical, as defined herein, attached to an alkyl radical, as defined herein.

[0048] The term "heteroatom" refers to any atom that is not carbon or hydrogen. Exemplary heteroatoms include, but are not limited to, nitrogen, oxygen, sulfur, phosphorus, boron, and the like.

[0049] The term "functional finishing dye" refers to a dye containing at least one functional finishing group covalently attached to the dye via a chemical linkage.

[0050] The term "functional finishing group" refers to a moiety that is present in a functional finishing dye which imparts a particular functional property to the dye-treated polymer.

[0051] The term "functional property" or "functionality," as used herein, refers to a particular non-inherent and/or enhanced physical property of the polymer due to the presence of a functional finishing group. Exemplary functional properties include, but are not limited to, antimicrobial, anti-static, softening, water-repellent, fire-resistant, soil-repellent, anti-UV, and anti-chemical properties, as well as a combination of two or more properties thereof.

[0052] "Leaving group" has the meaning conventionally associated with it in synthetic organic chemistry, *i.e.*, an atom or a group capable of being displaced by a nucleophile, and includes halo (such as chloro, bromo, and iodo), alkanesulfonyloxy, arenesulfonyloxy, alkylcarbonyloxy (*e.g.*, acetoxy), arylcarbonyloxy, mesyloxy, tosyloxy, trifluoromethanesulfonyloxy, aryloxy (*e.g.*, 2,4-dinitrophenoxy), methoxy, N,O-dimethylhydroxylamino, and the like.

[0053] The terms "antimicrobial," "microbicidal," or "biocidal" as used herein, refer to the ability to kill at least some types of microorganisms, or to inhibit the growth or reproduction of at least some types of microorganisms. The polymers prepared in accordance with the present invention have microbicidal (*i.e.*, antimicrobial) activity against a broad spectrum of pathogenic microorganisms. For example, if the polymer is a textile, the textiles have microbicidal activity against representative gram-positive (*e.g.*, *Staphylococcus aureus*) and gram-negative (*e.g.*, *Escherichia coli*) bacteria.

[0054] The term "quaternary ammonium salt group" refers to an amphipathic molecule that contains both a hydrophilic portion and a hydrophobic portion and is covalently attached to a dye. Preferably, the quaternary ammonium salt group has the formula:

$$-N(R^3)-L-N^+(R^4)(R^5)(R^6)\cdot X^-, \qquad \textbf{Ia}$$

wherein:

R^3 is a member selected from the group consisting of hydrogen, an alkyl group, and an amino protecting group;

each of R^4, R^5, and R^6 is independently selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl, and cycloalkylalkyl;

L is a linker comprising a 1-12 carbon atom chain; and

X is a counter anion.

[0055] As used herein, the term "treating," "contacting," or "reacting" refers to adding or mixing two or more reagents under appropriate conditions to produce the indicated and/or the desired product. It should be appreciated that the reaction which produces the indicated and/or the desired product may not necessarily result directly from the combination of two reagents which were initially added, *i.e.*, there may be one or more intermediates which are produced in the mixture which ultimately leads to the formation of the indicated and/or the desired product.

II. General Overview

[0056] The present invention provides novel functional finishing dyes comprising at least one functional finishing group covalently attached to a traditional dye via a chemical linkage. More particularly, the present invention provides novel antimicrobial cationic dyes comprising a quaternary ammonium salt (QAS) group covalently attached to an aminoanthraquinioid dye via a linker. The dyes are particularly useful for imparting a

functional property to a polymer, such as an antimicrobial, anti-static, softening, water-repellent, fire-resistant, soil-repellent, anti-UV, or anti-chemical property, and for simultaneously dyeing and finishing a polymer.

[0057] Conventional functional finishing of polymers typically require a separate process of dyeing and functional finishing. In contrast, the functional finishing dyes of the present invention allow dyeing and functional finishing to be achieved simultaneously, thereby reducing the amount of solvent used and the amount of waste solvent generated. Moreover, simultaneous dyeing and functional finishing of polymers reduces the amount of labor and time required to produce such treated polymers. These advantages result in the overall cost reduction in dyeing and treating polymers.

III. Polymers

[0058] Numerous polymers can be modified using the methods of the present invention. Polymers suitable for use in the present invention include, but are not limited to, textiles. Suitable textiles include, without limitation, fibers from plants, polymers from animals, natural organic polymers, synthetic organic polymers, inorganic substances, and combinations thereof. In particular, the textile is selected from the group consisting of fibers from plants such as cellulose, cotton, linen, hemp, jute, wood pulp, paper, and ramie; polymers derived from animals such as wool, mohair, vicuna, and silk; manufactured fibers that are based on natural organic polymers such as rayon, lyocell, acetate, triacetate, and azlon; synthetic organic polymers such as nylon, polyester, a polyester/cellulose blend, acrylic, aramid, olefin, spandex, vinyon, vinyl, graphite, an aromatic polyamide; inorganic substances such as glass, a metallic material, and a ceramic material; and combinations thereof.

[0059] Various textiles are preferred to practice the invention. These include, but are not limited to, a fiber, a yarn, or a natural or synthetic fabric. Various fabrics include, but are not limited to, a nylon fabric, a polyester fabric, an acrylic fabric, NOMEX®, KEVLAR®, a triacetate fabric, an acetate fabric, a cotton fabric, a wool fabric, and a fabric that is made from a combination of two or more materials thereof. NOMEX® is made of an aromatic polyamide material and is available from DuPont (Wilmington, Delaware). NOMEX® is used in fire fighting equipment.

[0060] As used herein, the term "acrylic fiber" refers to any manmade fiber derived from acrylic resins comprising a minimum of 85% acrylonitrile. Acrylic fiber is a

manufactured fiber in which the fiber forming substance is any long-chain synthetic polymer comprising at least 85% by weight of acrylonitrile units $(-CH_2-CH[CN]-)_x$. Suitable acrylic fibers for use in the present invention include, but are not limited to, Orlon®, MicroSupreme®, Cresloft™, Creslan® Plus, BioFresh™, WeatherBloc™ (commercially available from Sterling Fibers, Inc.), Dralon™ (commercially available from Bayer Inc.), Acrilan®, Bounce-Back®, Duraspun®, Pil-Trol®, Sayelle®, Sno-Brite™, The Smart Yarns®, Wear-Dated®, Wintuk® (commercially available from Solutia Inc.), Acrilin® acrylic, Dolan®, Dralon®, Vinyon N®, Dynel®, Verel®, and SEF modacrylic®. Those of skill in the art will know of other manufactures and trade names of acrylic fibers suitable for use in the present invention.

[0061] Additional polymers suitable for use in the present invention include, but are not limited to, plastics, rubber, paint, a surface coating, an adhesive, and a combination of two or more thereof. Suitable plastics include, without limitation, polyethylene, polypropylene, polystyrene, polyvinylchloride, polyamideimide, polyethersulfone, polyarylsulfone, polyetherimide, polyarylate, polysulfone, polycarbonate, polyetherketone, polyetheretherketone, polytetrafluoroethylene, nylon-6,6, nylon-6,12, nylon-11, nylon-12, and acetal resin plastic materials, as well as combinations thereof.

[0062] Considering the antimicrobial and anti-static properties imparted to the finished textiles prepared according to the methods and compositions set forth herein, those of skill in the art will readily appreciate that such finished textiles can advantageously be used in the preparation of the following articles/garments: surgeon's gowns, caps, masks, surgical covers, patient drapes, carpeting, bedding materials, underwear, socks, uniforms, and the like. Those of skill in the art will also readily appreciate that the finished textiles of the present invention can advantageously be used for a variety of other purposes, such as in hotel-use towels, bedding materials, hygienic products, clothing to protect against pesticides and other toxic chemicals, and the like.

IV. Functional Finishing Dyes

[0063] The functional finishing dyes of the present invention are comprised of a functional finishing group covalently attached to a dye moiety via a linker (*see,* Figure 1). However, those of skill in the art will readily appreciate that the functional finishing group can be covalently attached to the dye moiety without the use of a linker.

[0064] Any one of a variety of dyes are known to one skilled in the art is suitable for use in the present invention. Suitable dyes include, without limitation, cationic dyes such as

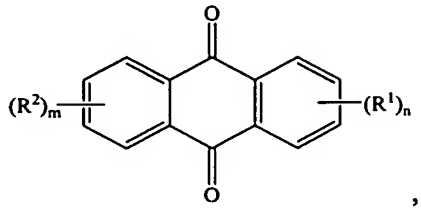
basic red 9, basic blue 9, basic blue 69, basic blue 22, basic orange 14, basic green 1, basic yellow 1, basic violet 2, basic brown 1, and other basic dyes; acid dyes such as an Acid Black dye, an Acid Blue dye, an Acid Orange dye, an Acid Red dye, an Acid Violet dye, and an Acid Yellow dye; disperse dyes such as Disperse Blue 1, Disperse Yellow 7 and Disperse Yellow 9; and combinations thereof. Direct dyes and reactive dyes are also suitable for use in the present invention. In a particularly preferred embodiment, the dye is an aminoanthraquinioid dye such as 1-aminoanthraquinone and 1,4-diaminoanthraquinone.

[0065] Suitable functional finishing groups are also well known to those skilled in the art. The functional finishing group imparts a particular non-inherent and/or enhanced physical property, *i.e.*, a functional property, to the polymer. Exemplary functional properties include, but are not limited to, antimicrobial, anti-static, softening, water-repellent, fire-resistant, soil-repellent, anti-UV, and anti-chemical properties, as well as a combination of two or more properties thereof. In a particularly preferred embodiment, the functional finishing group is a quaternary ammonium salt group that imparts antimicrobial and/or anti-static properties to the polymer.

[0066] By covalently linking dyes to functional finishing groups, a wide variety of functional finishing dyes can be prepared in accordance with the present invention. Such functional finishing dyes allow polymers (*e.g.*, textile materials) to be dyed and functionalized simultaneously in a single treatment process, thereby reducing the overall cost and time for producing dyed and functionalized polymers.

[0067] The presence of a linker between the dye and the functional finishing group can be optional depending on the reactive groups that are present on the dye and the functional finishing group. For example, if complementary reactive groups are present in the dye and the functional finishing group, they can be covalently attached without the need for any additional linker. However, if the reactive groups that are present in the dye and the functional finishing group are not complementary reactive groups, one of the reactive groups can be converted to a complementary reactive group, or a linker having appropriate complementary reactive groups can be used to covalently link the dye and the functional finishing group. In a preferred embodiment, the linker comprises a 1-12 carbon atom chain that can be interrupted with one or more heteroatoms. Suitable carbon atom chains include, without limitation, an alkylene group, a -C(O)R group, wherein R is an an alkylene group, and an alkylamino group.

[0068] In one aspect, the functional finishing dye is a QAS-aminoanthraquinioid dye conjugate, *i.e.*, QAS-dye, having the formula:



I

wherein:

each R^1 is an independently selected quaternary ammonium salt group;

each R^2 is independently selected from a quaternary ammonium salt group and a substituent group;

m is an integer from 0 to 4; and

n is an integer from 1 to 4.

[0069] In one embodiment, the quaternary ammonium salt group has the formula:

$$-N(R^3)-L-N^+(R^4)(R^5)(R^6)\cdot X^-,$$

Ia

wherein:

R^3 is a member selected from the group consisting of hydrogen, an alkyl group, and an amino protecting group;

each of R^4, R^5, and R^6 is independently selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloalkyl, and cycloalkylalkyl;

L is a linker comprising a 1-12 carbon atom chain; and

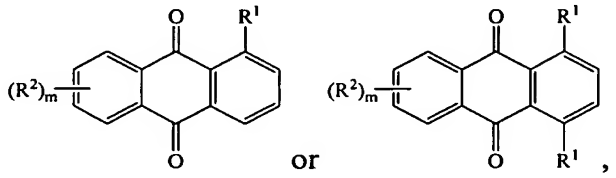
X is a counter anion.

[0070] In another embodiment, the R^4 and R^5 groups in the quaternary ammonium salt group are each independently selected C_1-C_4 alkyl groups, and R^6 is a C_4-C_{18} alkyl group. In a preferred embodiment, the R^4 and R^5 groups in the quaternary ammonium salt group are methyl groups, and R^6 is a C_4-C_{18} alkyl group. Suitable R^6 groups include, for example, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl groups. In a particularly preferred embodiment, the R^6 group is an octyl or a dodecyl group.

[0071] In yet another embodiment, X is independently selected from the group consisting of F^-, Cl^-, Br^-, I^-, and combinations thereof. In still yet another embodiment, the substituent group is independently selected from the group consisting of hydrogen, alkyl,

aryl, aralkyl, cycloalkyl, cycloalkylalkyl, sulfonate, hydroxyl, alkoxyl, amino, and alkylamino groups. In a further embodiment, m is 0.

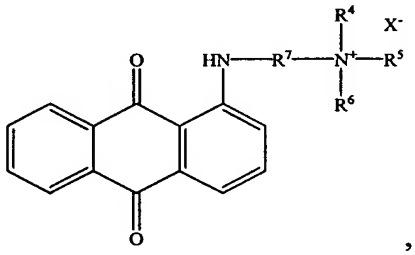
[0072] In another embodiment, n is 1 or 2. Within this group of compounds, a particularly preferred compound of formula **I** is of the formula:



IIa or **IIb**,

wherein R^1, R^2, and m are as defined above.

[0073] In a preferred embodiment, the compound of formula **IIa** has the following structure:



wherein:

R^4 and R^5 are each independently selected C_1-C_4 alkyl groups;

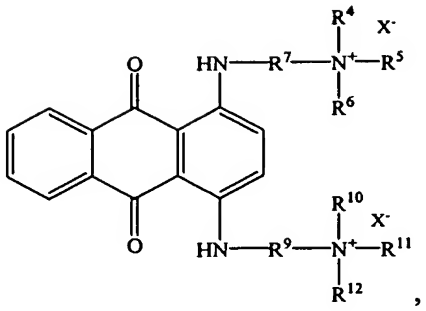
R^6 is a C_4-C_{18} alkyl group;

R^7 is a C_1-C_{12} alkylene group optionally interrupted with a heteroatom or a -C(O)R^8 group, wherein R^8 is a C_1-C_{12} alkylene group; and

X is a counter anion.

[0074] In one embodiment, R^4 and R^5 are methyl groups. In a second embodiment, R^6 is an octyl or a dodecyl group. In a third embodiment, R^7 is a -CH_2 or a -C(O)CH_2 group. In a fourth embodiment, X is independently selected from the group consisting of F^-, Cl^-, Br^-, I^-, and combinations thereof.

[0075] In another preferred embodiment, the compound of formula **IIb** has the following structure:



wherein

R^4, R^5, R^{10}, and R^{11} are each independently selected C_1-C_4 alkyl groups;

R^6 and R^{12} are each independently selected C_4-C_{18} alkyl groups;

R^7 and R^9 are each independently selected C_1-C_{12} alkylene groups optionally interrupted with a heteroatom or -C(O)R^8 groups, wherein R^8 is a C_1-C_{12} alkylene group; and

each X is an independently selected counter anion.

[0076] In one embodiment, R^4, R^5, R^{10}, and R^{11} are methyl groups. In a second embodiment, R^6 and R^{12} are independently selected octyl or dodecyl groups. In a third embodiment, R^7 and R^9 and independently selected -CH_2 or -C(O)CH_2 groups. In a fourth embodiment, X is independently selected from the group consisting of F^-, Cl^-, Br^-, I^-, and combinations thereof.

[0077] Figure 2A shows various structures of the antimicrobial QAS-dyes according to one embodiment of the present invention.

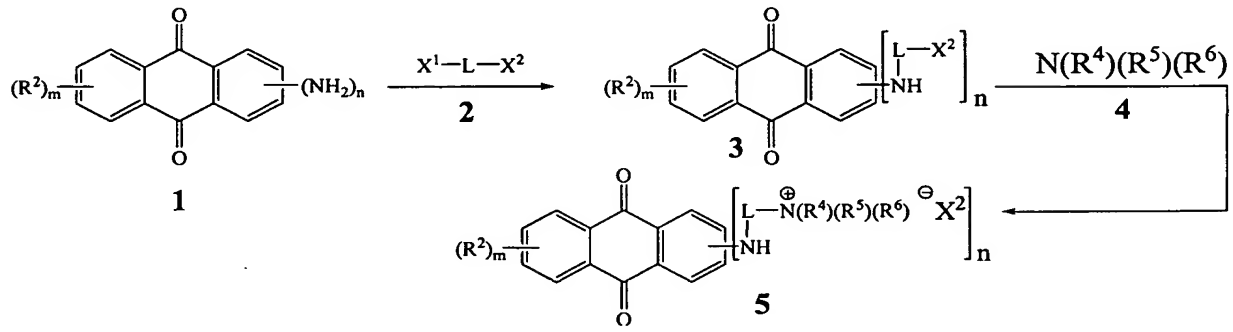
V. Synthesis

[0078] The functional finishing dyes of the present invention can be prepared by a variety of methods known to one skilled in the art, including, without limitation, solid-phase, solution-phase, and combinatorial synthesis. It should be appreciated that although the following schemes for producing compounds of Formula **I** often indicate exact structures, methods of the present invention apply widely to analogous compounds of Formula **I** as well as to other dyes known to one skilled in the art given an appropriate consideration to protection and deprotection of reactive functional groups by methods standard to the art of organic chemistry. For example, in order to prevent unwanted side reactions, hydroxyl groups sometimes need to be converted to ethers or esters during chemical reactions at other sites in the molecule. The hydroxyl protecting group is then removed to provide the free hydroxyl group. Similarly, amino groups and carboxylic acid groups can be derivatized to

protect them against unwanted side reactions. Typical protecting groups, and methods for attaching and cleaving them, are described fully in, for example, T.W. Greene and P.G.M. Wuts, *Protective Groups in Organic Synthesis*, 3rd edition, John Wiley & Sons, New York, 1999, and Harrison and Harrison et al., *Compendium of Synthetic Organic Methods*, Vols. 1-8 (John Wiley and Sons, 1971-1996), which are incorporated herein by reference in their entirety.

[0079] As described above, the presence of a linker between the dye and the functional finishing group is optional depending on the reactive groups that are present on the dye and the functional finishing group. The following is intended to be a mere illustration of one particular synthetic strategy that can be employed in producing the functional finishing dyes of the present invention. It should be appreciated that methods for preparing functional finishing dyes are not limited to those specifically disclosed herein as one skilled in the art can readily adapt other synthetic strategies and chemical reactions that are generally known to such a skilled artisan to derive other functional finishing dyes.

[0080] Methods for preparing functional finishing dyes will now be illustrated with respect to preparing compounds of Formulas **IIa** and **IIb**, wherein R^1 is a quaternary ammonium salt group of Formula **Ia**. As shown in Scheme **I** below, an anthraquinone compound **1** having one or more amino functional groups is reacted with a linker compound **2** to produce a di-substituted aminoanthraquinone **3**.



Scheme **I**

[0081] The linker compound **2** comprises two different reactive functional groups such that one of the reactive functional group reacts preferentially with the amino group of the anthraquinone compound **1**. For example, the linker compound **2** can comprise an activated acyl group, *e.g.*, acyl halide, alkyl halide, epoxide, or anhydride, and a leaving group for a nucleophilic substitution reaction. In this manner, the activated acyl group, *i.e.*, X^1, reacts preferentially with the amino group. Suitable reaction conditions for coupling an

amino group with an activated acyl group are well known to one skilled in the art and typically involve reacting the two groups at reduced temperature, *e.g.*, 0°C. A base and/or a coupling catalyst can optionally be added to the reaction mixture to neutralize any acid that may be generated and/or to facilitate the coupling reaction, respectively.

[0082] The di-substituted aminoanthraquinone **3** can optionally be purified prior to reacting with a tri-substituted amine compound **4** to produce a quaternary ammonium salt substituted anthraquinone **5**. Unlike the first coupling reaction which involves an acyl transfer reaction, this second coupling reaction typically involves a nucleophilic substitution reaction where the amino group of the tri-substituted amine compound **4** displaces the leaving group X^2 on the di-substituted aminoanthraquinone **3**. Suitable reaction conditions for a nucleophilic substitution reaction are known to one skilled in the art and often involve elevated reaction temperatures, *i.e.*, >25°C and preferably >50°C.

[0083] While the above reactions have been described in a particular order of producing the quaternary ammonium salt substituted anthraquinone **5**, it should be appreciated that methods for producing such a compound is not limited to this particular order. For example, by selecting appropriate reactive groups X^1 and X^2, the linking group **2** can be reacted first with the tri-substituted amine compound **4**, and then the resulting product can be reacted with the anthraquinone compound **1**.

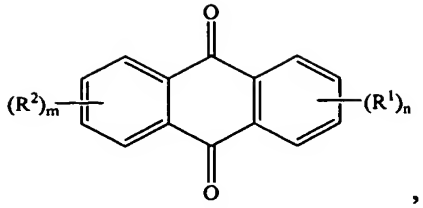
[0084] Figure 3 shows a representative synthetic scheme for the mono-QAS substituted dyes of the present invention.

VI. Polymer Coating

[0085] The present invention also provides a polymer that is coated with the functionalized finishing dyes described above. As such, in another aspect, the present invention provides a polymer composition comprising:

(a) a polymer, wherein the polymer is a member selected from the group consisting of a textile, a plastic, rubber, paint, a surface coating, an adhesive, and a combination thereof; and

(b) a compound having the formula:



I

wherein:

each R^1 is an independently selected quaternary ammonium salt group;

each R^2 is independently selected from a quaternary ammonium salt group and a substituent group;

m is an integer from 0 to 4; and

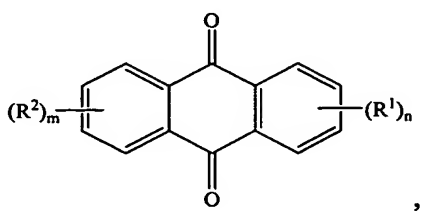
n is an integer from 1 to 4.

[0086] Such polymers can be readily prepared using any one of conventional dyeing processes known to one skilled in the art. However, unlike conventional dyeing processes, methods of the present invention utilize the functional finishing dye described herein. In this manner, what is typically a two-step process of dyeing and finishing a polymer is achieved in a single process, thereby significantly reducing the overall cost and time.

[0087] In general, methods for treating a polymer are similar to other conventional dyeing processes. Thus, a polymer to be treated is immersed in a treating solution, typically an aqueous solution. The treating solution comprises a functional finishing dye of the present invention. The polymer is immersed in the treating solution for a period of time and under conditions appropriate to achieve a sufficient amount of polymer coating to produce a desired or favorable functional finishing dye-coated polymer, *i.e.,* dye-treated polymer. The treated polymer is removed from the treating solution and dried.

[0088] As such, in yet another aspect, the present invention provides a method for simultaneously dyeing and finishing a polymer, the method comprising:

immersing the polymer in an aqueous treating solution which comprises a compound having the formula:



,

I

wherein:

each R^1 is an independently selected quaternary ammonium salt group;

each R^2 is independently selected from a quaternary ammonium salt group and a substituent group;

m is an integer from 0 to 4; and

n is an integer from 1 to 4.

[0089] In one embodiment, the method further comprises removing excess aqueous treating solution from the polymer. For example, the excess aqueous treating solution can be removed with or without washing the polymer. In another embodiment, the method further comprises drying the article after removing excess aqueous treating solution to produce a dried polymer. In yet another embodiment, the aqueous treating solution further comprises a wetting agent.

[0090] The term "wetting agent" as used herein refers to a substance that increases the rate at which a liquid spreads across the polymer surface, *i.e.,* it renders the polymer surface nonrepellent to a liquid. Examples of suitable wetting agents include, but are not limited to, Triton X-100 (Sigma Chemical Co., St. Louis, Mo.), SEQUAWET® (Sequa Chemical Inc., Chester, S.C.), and AMWET® (American Emulsions Co., Dalton, Ga.). Other wetting agents suitable for use in the present invention will be known to and used by those of skill in the art.

[0091] Other additives can also be present in the aqueous treating solution to impart additional characteristics to the polymer. Such additives include, but are not limited to, anti-static, softening, water-repellent, fire-resistant, soil-repellent, anti-UV, anti-chemical, and other antimicrobial agents, as well as a combination of two or more agents thereof. Other agents known to and used by those of skill in the art are also suitable additives. Examples of softeners which can be added to the aqueous treating solution include, but are not limited to, MYKON® and SEQUASOFT®, both of which are commercially available from Sequa Chemical Inc. (Chester, S.C.). Examples of water-repellent agents which can be added to the aqueous treating solution include, but are not limited to, SEQUAPEL® (Sequal Chemical Inc., Chester, S.C.), SCOTCHGARD (3M, St. Paul, Minn.), and other water-repellent finishing solutions known to and used by those of skill in the art.

[0092] Those of skill in the art will appreciate that the concentration of the various components of the treating solution can be varied widely depending on the particular

components employed and the results desired. Typically, the functional finishing dye is present at a concentration of at least about 0.5% wt/vol. (g/mL). More typically, the functional finishing dye is present at a concentration ranging from about 0.1% wt/vol. to about 10% wt/vol., preferably at a concentration ranging from about 0.5% to about 5%, and more preferably at a concentration ranging from about 0.5% to about 2%. It will be readily apparent to those of skill in the art that higher functional finishing dye concentrations (*e.g.*, 50% or more) can be employed, but such higher concentrations are not required to impart functionality to the polymer. Again, suitable functionality can be imparted using a functional finishing dye concentration as low as about 0.5%. The wetting agent is typically present at a concentration ranging from about 0.1% to about 3%, preferably at a concentration ranging from about 0.2% to about 1%. The pH of the treating solution will typically range from a pH of about 2 to about 6 and, preferably, from a pH of about 2.5 to about 4.5. In a particularly preferred embodiment, the pH of the treating solution is about 3.

[0093] As described above, the polymer is preferably a textile. The textile can be roving, yarn, or fabric regardless of whether spun, knit, or woven, or can be non-woven sheets or webs. Moreover, the textile can be made of cellulosic fibers, polyester fibers, or a blend of these. In addition, other polymer materials having reactive functional groups (*e.g.*, -OH groups) can be used. Such polymer materials include, but are not limited to, polyvinyl alcohol (PVA), starches, and proteins. In wetting the textile in the finishing or treating bath, ordinary textile equipment and methods suitable for batchwise or continuous passage of roving, yarns, or fabrics through an aqueous solution can be used, at any speed permitting thorough and uniform wetting of the textile material.

[0094] The excess treating solution can be removed by ordinary mechanical methods such as by passing the treated polymer between squeeze rolls, by centrifugation, by draining, or by padding. In a preferred embodiment, the excess treating solution is removed by padding.

[0095] The treated polymer is then typically dried at a temperature ranging from about 50°C to about 90°C, and more preferably at a temperature ranging from about 75°C to about 85°C for a period of time ranging from about 3 to about 8 minutes, preferably for about 5 minutes. Drying of treated polymer can be carried out using any ordinary means such as oven drying, line drying, or tumble drying in a mechanical clothes dryer.

[0096] In still yet another aspect, the present invention provides a composition for finishing polymers such as textiles. The composition comprises a functional finishing dye described herein. In addition, the composition can also include a wetting agent. In a preferred embodiment, the composition further includes one or more additives to impart favorable characteristics. The description above pertaining to the functional finishing dyes, wetting agents, additives, and their various concentrations are fully applicable to this composition and, thus, such discussions will not be repeated again. The pH of the composition typically range from a pH of about 2 to about 6, and preferably from a pH of about 2.5 to about 4.5. Those of skill in the art will readily appreciate that the above composition can be prepared in a concentrated form or, alternatively, in a form suitable for immediate use, *i.e.*, at appropriate reagent concentrations.

VII. Utility

[0097] Quaternary ammonium salts (QAS) are antimicrobial compounds. QAS inactivate microorganisms by disturbing their cytoplasmic membrane and have been widely used as surface disinfectants and antimicrobial finishing agents in textiles. *See,* for example, Kim *et al.*, *Textile Res. J.*; 70:728 (2000); Kim *et al.*, *Textile Res. J.;* 71:318 (2001); and Latlief *et al.*, *J. Pediatrics*; 39:730 (1951). Meanwhile, anthraquinioid structures are excellent chromophores and have been widely used as dyes. Therefore, by incorporating both QAS and anthraquinone structures, compounds of Formula **I** can be used simultaneously as dyes and functional finishing groups.

[0098] Accordingly, the polymers treated with a compound of formula **I** have microbiocidal activity against a broad spectrum of pathogenic microorganisms. For example, such polymers have microbiocidal activity against representative gram-positive (*e.g., Staphylococcus aureus*) and gram-negative bacteria (*e.g., Escherichia coli*).

[0099] Considering the antimicrobial and anti-static properties imparted to the finished textiles prepared according to the methods and compositions set forth herein, those of skill in the art will readily appreciate that such finished textiles can advantageously be used in the preparation of the following articles/garments: surgeon's gowns, caps, masks, surgical covers, patient drapes, carpeting, bedding materials, underwear, socks, uniforms, and the like. Those of skill in the art will also readily appreciate that the finished textiles of the present invention can advantageously be used for a variety of other purposes, such as in

hotel-use towels, bedding materials, hygienic products, clothing to protect against pesticides and other toxic chemicals, and the like.

[0100] Numerous applications for the treated polymers of the present invention exist. For instance, the polymers can be used as microbiocidal protective clothing for personnel in the medical field as well as in related healthcare and hygiene areas.

[0101] In addition, the functional properties of the dyes of the present invention can be imparted to carpeting materials to create odor-free and germ-free carpets. Moreover, all germ-free environments, such as those required in biotechnology and in the pharmaceutical industry, can benefit from the use of the microbicidal polymers of the present invention to prevent any contamination from air, liquid, and/or solid media.

[0102] The treated polymers of the present invention are effective against a wide range of microorganisms including, but not limited to, bacteria, protozoa, fungi, viruses and algae. Moreover, the treated polymers described herein can be employed in a variety of disinfecting applications, such as water purification. They will be of importance in controlling microbiological contamination or growth of undesirable organisms in the medical and food industries. In addition, they can be used as preservatives and preventatives against microbiological contamination in paints, coatings, and on surfaces.

[0103] The invention will be described in greater detail by way of specific examples. The following examples are offered for illustrative purposes, and are intended neither to limit or define the invention in any manner.

VIII. Examples

Materials and instrumentation

[0104] 1,4-diaminoanthraquinone (90%, Aldrich) was purified by repeated crystallization from acetone. 1-aminoanthraquinone (97%, Aldrich), chloroacetyl chloride (98%, Acros), *N,N*-dimethylbutylamine (99%, Aldrich), *N,N*-dimethyloctylamine (97%, Acros), *N,N*-dimethyldodecylamine (95%, Acros) were used as received.

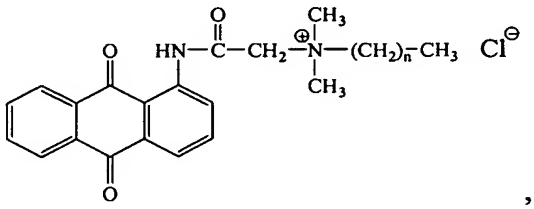
[0105] The melting points of the samples were measured using a Shimadzu DSC-50 instrument at a heating rate of 10°C min^{-1} under a N_2 atmosphere. FTIR spectra were taken on a Nicolet Magana IR-560 spectrometer using KBr pellets. The samples were made thin enough to ensure that the Beer-Lambert law was obeyed. ^{1}H-NMR and ^{13}C-NMR spectra

were recorded on a Varian Mercury 300 spectrometer. Electronic absorption spectra were recorded on a Hitachi U-2000 spectrophotometer.

[0106] Acetylation of the α-aminoanthraquinioid (AQ) group was achieved according to the procedures disclosed by Martelli et al. in *J. Med.Chem.*; 31(10):1956 (1988). The second step was a quaternization of the primary chloride with different tertiary amines. The synthetic procedure is outlined in Figure 3. The structures of the compounds prepared are presented in Figure 2B.

Example 1

[0107] This example illustrates the synthesis of a compound having the formula:



, where n is 3.

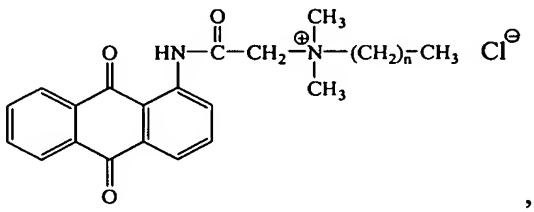
m-4

[0108] A solution of 1-aminoanthraquinone (0.01 mole) in 30 mL of dimethylacetamide was cooled to 0 °C, and 5 mL (0.06 mole) chloroacetyl chloride in 150 mL of chloroform was slowly added with vigorous stirring. The reaction mixture was further stirred for one hour at room temperature and the solvent was evaporated under vacuum. The product was precipitated by addition of ethyl ether. The crude product (1-chloroacetamido-9,10-anthracenedione) was purified by recrystallization from *N,N*-dimethylformamide (DMF) with a yield of 78%. After acetylation, a suspension of 0.01 mole (1-chloroacetamido-9,10-anthracenedione) in 200 mL of DMF, together with 0.1 mole *N,N*-dimethylbutylamine, was heated at 95 °C for three hours. After removing DMF under reduced pressure, the product was purified from an ethyl ether-ethyl alcohol solvent mixture. Yield: 65 %. Melting point: 219 °C. IR spectra data (KBr): $\nu_{\text{-NH-CO-}}$=1700 cm^{-1}. ^{1}H-NMR spectra data ($CDCl_3$, δ): 12.597 (singlet, 1H, -N<u>H</u>-CO-); 8.663~8.696, 8.102~8.159, 7.958~7.987, 7.573~7.721 (multiplet, multiplet, multiplet, multiplet, 7H, protons attached to C_2,C_3, C_4, C_5, C_6, C_7, C_8); 5.578 (singlet, 2H, -CO-C<u>H</u>$_2$-$N^+(CH_3)_2C_4H_9$), 3.914~3.970 (broad multiplet, 2H, -$N^+(CH_3)_2$-C<u>H</u>$_2$-C_3H_7), 3.757 (singlet, 6H, -N^+(C<u>H</u>$_3$)$_2$-CH_2-C_3H_7), 1.857 (broad multiplet, 2H, -$N^+(CH_3)_2$-CH_2-C<u>H</u>$_2$-C_2H_5), 1.438~1.510 (multiplet, 2H, -$N^+(CH_3)_2$-CH_2-CH2-C<u>H</u>2-CH_3),

0.997~1.046 (triplet, 3H, $-N^+(CH_3)_2-CH_2-CH_2-CH_2-C\underline{H}_3$). λ_{max} = 379 nm. Molar absorptivity (ε_{max}) = 1,895 $L\cdot mol^{-1}\cdot cm^{-1}$.

Example 2

[0109] This example illustrates the synthesis of a compound having the formula:



, where n is 7.

m-8

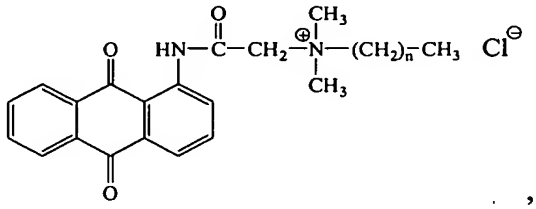
[0110] This compound was prepared using the procedure of Example 1 by substituting *N,N*-dimethylbutylamine with *N,N*-dimethyloctylamine. Yield: 62%. Melting point: 205°C. IR spectra data (KBr): $\nu_{-NH-CO-}$=1705 cm^{-1}. ^{1}H-NMR spectra data ($CDCl_3$, δ): 12.552 (singlet, 1H, -N<u>H</u>-CO-); 8.612~8.636, 7.990~8.091, 7.863~7.889, 7.506~7.668 (multiplet, multiplet, multiplet, multiplet, 7H, protons attached to C_2,C_3, C_4, C_5, C_6, C_7, C_8); 5.683 (singlet, 2H, $-CO-C\underline{H}_2-N^+(CH_3)_2C_8H_{17}$), 3.905~3.980 (broad multiplet, 2H, $-N^+(CH_3)_2-C\underline{H}_2-C_7H_{15}$), 3.778 (singlet, 6H, $-N^+(C\underline{H}_3)_2-CH_2-C_7H_{15}$), 1.827 (broad peak, 2H, $-N^+(CH_3)_2-CH_2-C\underline{H}_2-C_6H_{13}$), 1.383, 1.251 (broad peaks, 10H, $-N^+(CH_3)_2-CH_2-C\underline{H}_2-(C\underline{H}_2)_5-CH_3$), 0.831~0.853 (triplet, 3H, $-N^+(CH_3)_2-CH_2-CH_2-(CH_2)_5-C\underline{H}_3$). λ_{max} = 379 nm. ε_{max} = 1,880 $L\cdot mol^{-1}\cdot cm^{-1}$.

[0111] The chemical structure of m-8 was further confirmed by ^{1}H and ^{13}C NMR analysis. As shown in the ^{1}H spectrum of Figure 4, the multiple peaks in the region of δ 7.506~8.612 ppm are assigned to aromatic protons (Silverstein *et al.*, *Spectrometric identification of organic compounds*, New York: John Wiley & Sons, Inc. (1998)). Additionally, several characteristic peaks of the dyes can also be found. For example, the peak centered at 12.552 ppm is the amide proton (H_a), and the signal at 5.683 ppm can be attributed to H_b. In the ^{13}C spectrum (Figure 5), the peaks at 186.312 and 181.847 ppm are assigned to the two carbonyl carbons in the anthraquinone structure. The amide carbon appears at 163.984 ppm. The twelve peaks in the range of 100~140 ppm are caused by the aromatic carbons, and the ten peaks within 10~70 ppm correspond to the eleven alkyl carbons, which are located in ten different chemical environments. All of these findings

indicate that cationic dye-QAS compounds of the present invention can be readily synthesized following the reaction scheme shown in Figure 3.

Example 3

[0112] This example illustrates the synthesis of a compound having the formula:



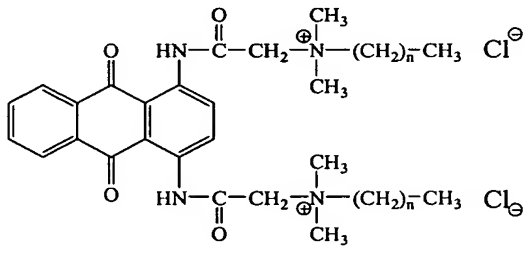
, where n is 11.

m-12

[0113] This compound was prepared using the procedure of Example 1 by substituting *N,N*-dimethylbutylamine with *N,N*-dimethyldodecylamine. Yield: 65%. Melting point: 206°C. IR spectra data (KBr): $\nu_{\text{-NH-CO-}}$=1705 cm^{-1}. ^{1}H-NMR spectra data ($CDCl_3$, δ): 12.552 (singlet, 1H, -NH-CO-); 8.577~8.606, 7.975~8.065, 7.839~7.864, 7.454~7.664 (doublet, multiplet, doublet, multiplet, 7H, protons attached to C_2,C_3, C_4, C_5, C_6, C_7, C_8); 5.648 (singlet, 2H, -CO-C<u>H</u>$_2$-$N^+(CH_3)_2C_{12}H_{25}$), 3.905~3.980 (broad multiplet, 2H, -$N^+(CH_3)_2$-C<u>H</u>$_2$-$C_{11}H_{23}$), 3.769 (singlet, 6H, -N^+(C<u>H</u>$_3$)$_2$-CH_2-$C_{11}H_{23}$), 1.857 (broad peak, 2H, -$N^+(CH_3)_2$-CH_2-C<u>H</u>$_2$-$C_{10}H_{21}$), 1.340, 1.191 (broad peaks, 18H, -$N^+(CH_3)_2$-CH_2-C<u>H</u>$_2$-(C<u>H</u>$_2$)$_9$-CH_3), 0.829 (triplet, 3H, -$N^+(CH_3)_2$-CH_2-CH_2-$(CH_2)_9$-C<u>H</u>$_3$). λ_{max} = 379 nm. ε_{max} = 1,626 $L \cdot mol^{-1} \cdot cm^{-1}$.

Example 4

[0114] This example illustrates the synthesis of a compound having the formula:



, where n is 3.

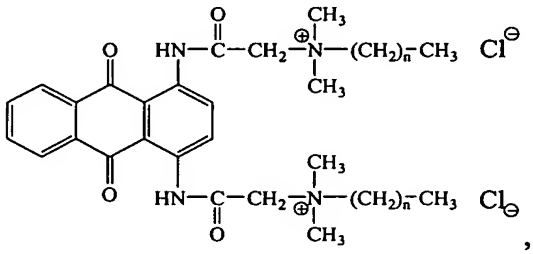
bi-4

[0115] A solution of 0.01 mole of 1,4-diaminoanthraquinone in 30 mL of dimethylacetamide at 0°C was reacted with 0.12 mole chloroacetyl chloride in 300 mL of

chloroform to yield 76% of 1,4-bis(chloroacetamido)-9,10-anthracenedione. A suspension of 0.01 mole 1,4-bis(chloroacetamido)-9,10-anthracenedione in 300 mL of DMF, together with 0.2 mole N,N-dimethylbutylamine was heated at 95 °C for three hours. The final product was purified by crystallization using an ethyl ether-ethyl alcohol solvent mixture. Yield: 62%. Melting point: 221 °C. IR spectra data (KBr): $\nu_{\text{-NH-CO-}}$=1705 cm^{-1}. ^{1}H-NMR spectra data ($CDCl_3$, δ): 12.611 (singlet, 2H, -N<u>H</u>-CO-); 8.021, 7.959~7.989, 7.671~7.700 (singlet, multiplet, multiplet, 6H, protons attached to C_2, C_3, C_5, C_6, C_7, C_8); 5.962 (singlet, 4H, -CO-C<u>H</u>$_2$-$N^+(CH_3)_2C_4H_9$), 3.972~4.029 (broad multiplet, 4H, -$N^+(CH_3)_2$-C<u>H</u>$_2$-C_3H_7), 3.790 (singlet, 12H, -N^+(C<u>H</u>$_3$)$_2$-CH_2-C_3H_7), 1.916 (broad peak, 4H, -$N^+(CH_3)_2$-CH_2-C<u>H</u>$_2$-C_2H_5), 1.478~1.528, 1.191 (multiplet, 4H, -$N^+(CH_3)_2$-CH_2-C<u>H</u>$_2$-C<u>H</u>$_2$-CH_3), 1.014~1.063 (Triplet, 6H, -$N^+(CH_3)_2$-CH_2-CH_2-CH_2-C<u>H</u>$_3$). λ_{max} = 431 nm. ε_{max} = 2,043 L·mol^{-1}·cm^{-1}.

Example 5

[0116] This example illustrates the synthesis of a compound having the formula:



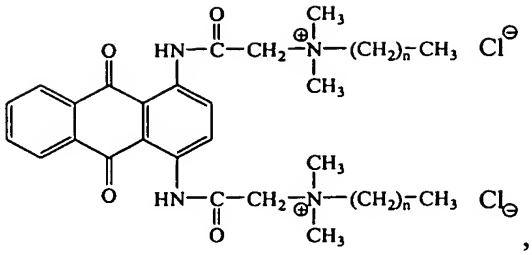
, where n is 7.

bi-8

[0117] This compound was prepared using the procedure of Example 4 by substituting *N,N*-dimethylbutylamine with *N,N*-dimethyloctylamine. Yield: 65%. Melting point: 235°C. IR spectra data (KBr): $\nu_{\text{-NH-CO-}}$=1706 cm^{-1}. ^{1}H-NMR spectra data ($CDCl_3$, δ): 12.545 (singlet, 2H, -N<u>H</u>-CO-); 7.939~7.969, 7.648~7.678 (triplet, multiplet, 6H, protons attached to C_2, C_3, C_5, C_6, C_7, C_8); 5.927 (singlet, 4H, -CO-C<u>H</u>$_2$-$N^+(CH_3)_2C_8H_{17}$), 3.986 (broad multiplet, 4H, -$N^+(CH_3)_2$-C<u>H</u>$_2$-C_7H_{15}), 3.778 (singlet, 12H, -N^+(C<u>H</u>$_3$)$_2$-CH_2-C_7H_{15}), 1.892 (broad peak, 4H, -$N^+(CH_3)_2$-CH_2-C<u>H</u>$_2$-C_6H_{13}), 1.396, 1.269 (broad peaks, 20H, -$N^+(CH_3)_2$-CH_2-C<u>H</u>$_2$-(C<u>H</u>$_2$)$_5$-CH_3), 0.845~0.968 (Triplet, 6H, -$N^+(CH_3)_2$-CH_2-CH_2-$(CH_2)_5$-C<u>H</u>$_3$). λ_{max} = 436 nm. ε_{max} = 2,001 L·mol^{-1}·cm^{-1}.

Example 6

[0118] This example illustrates the synthesis of a compound having the formula:



, where n is 11.

bi-12

[0119] This compound was prepared using the procedure of Example 4 by substituting *N,N*-dimethylbutylamine with *N,N*-dimethyldodecylamine. Yield: 60%. Melting point: 234°C. IR spectra data (KBr): $\nu_{\text{-NH-CO-}}$=1708 cm^{-1}. ^{1}H-NMR spectra data ($CDCl_3$, δ): 12.434 (singlet, 2H, -NH-CO-); 7.896, 7.865, 7.649 (multiplet, singlet, multiplet, 6H, protons attached to C_2, C_3, C_5, C_6, C_7, C_8); 5.846 (singlet, 4H, -CO-CH_2-$N^+(CH_3)_2C_{12}H_{25}$), 3.982 (broad multiplet, 4H, -$N^+(CH_3)_2$-CH_2-$C_{11}H_{23}$), 3.754 (singlet, 12H, -$N^+(CH_3)_2$-CH_2-$C_{11}H_{23}$), 1.899 (broad peak, 4H, -$N^+(CH_3)_2$-CH_2-CH_2-$C_{10}H_{21}$), 1.391, 1.243 (broad peaks, 36H, -$N^+(CH_3)_2$-CH_2-CH_2-$(CH_2)_9$-CH_3), 0.866 (Triplet, 6H, -$N^+(CH_3)_2$-CH_2-CH_2-$(CH_2)_9$-CH_3). λ_{max} = 449 nm. ε_{max} = 1,977 $L \cdot mol^{-1} \cdot cm^{-1}$.

Example 7

[0120] This example illustrates the antimicrobial activities of some of the representative compounds of Formula **I**.

[0121] The antimicrobial properties of some of the functional finishing dyes of Formula **I** were evaluated using a minimum inhibitory concentration (MIC). The MIC is the concentration at which no growth of bacteria was observed following such a procedure. *See,* for example, Kaminski *et al., J. Pharm. Sci.* 65(12):1737 (1976).

[0122] Briefly, determining the MIC involved placing 1 mL of an aqueous suspension containing 10^6-10^7 colony-forming units (CFU)/mL of *Staphylococcus aureus* (Gram-positive) or *Escherichia coli* (Gram-negative) into 9 mL of aqueous solutions containing different concentrations of the QAS-dyes of the present invention. After 24 hours, a 100 μL aliquot of the resultant solution was serially diluted by sterilized distilled water. 100 μL of the dilution was placed onto a nutrient agar plate and incubated at 37°C for 24 hours. The same procedure was applied to a distilled water solution without the compounds as a control. The MIC values of the QAS-dyes from Examples 1-6 against *S. aureus* and *E. coli* are shown in Table 1 below.

Table 1. The MIC of the compounds from Examples 1-6.

	Compound of Example:					
	1 (m-4)	2 (m-8)	3 (m-12)	4 (bi-4)	5 (bi-8)	6 (bi-12)
MIC *S. aureus* (ppm)	>800	80	20	800	60	20
MIC *E. coli* (ppm)	>800	50	20	600	20	20

MIC is expressed in ppm (parts per million) of the compound.

[0123] As shown in Table 1, all of the QAS-dyes displayed biocidal properties against both species of bacteria. Generally, the increase in alkyl chain length of the QAS resulted in higher antimicrobial activities. For example, the compound from Example 1 (*i.e.*, m-4) provided little effect even when a concentration higher than 800 ppm was used, and the compound from Example 4 (*i.e.*, bi-4) needed more than 600 ppm to achieve effective antimicrobial activity. However, the compounds from Examples 2, 3, 5, and 6 (*i.e.*, m-8, m-12, bi-8, and bi-12, respectively) provided a total kill of 10^6-10^7 CFU/mL of *S. aureus* or *E. coli* at concentrations lower than 100 ppm.

[0124] In general, the bi-QAS substituted dyes (*i.e.*, bi-4, bi-8, and bi-12) typically had higher antimicrobial activities than the mono-QAS substituted dyes (*i.e.*, m-4, m-8, and m-12). In addition, these compounds generally had better antimicrobial efficacy against gram-negative bacteria (*e.g.*, *E. coli*) than Gram-positive bacteria (*e.g.*, *S. aureus*).

Example 8

[0125] This example illustrates the Fourier Transform Infrared (FTIR) Spectra of some of the representative compounds of Formula **I**.

[0126] The FTIR spectra of the compounds from Examples 1-3 are shown in Figure 6. As a control, the starting material, 1-aminoanthraquinone (I_a), shows absorbance bands at 3416, 3298, and 1665 cm^{-1}, which can be attributed to the hydrogen-bonded primary amines and the C=O stretching band of the anthraquinone structures, respectively (Silverstein *et al.*, *Spectrometric identification of organic compounds*, New York: John Wiley & Sons, Inc. (1998)). However, in the region of 3200-3500 cm^{-1}, the crude product, 1-chloroacetamido-9,10-anthracenedione (I_b), as well as the compounds from Examples 1-3 (m-4, m-8, and m-12) only show one band at about 3430 cm^{-1}, indicating that the primary amine in I_a has been transformed into an amide. In addition, a new peak centered around 1690-1700 cm^{-1} can be observed in the spectra of I_b, m-4, m-8, and m-12, which is most likely produced by the carbonyl group of the amide structures. Furthermore, with an increase in the alkyl chain

length in the QAS, the intensity of the alkane absorption bands (2800-3000 cm^{-1}) also increased. Similar phenomena was observed in the FTIR spectra for the compounds from Examples 4-6 (bi-4, bi-8, and bi-12).

Example 9

[0127] This example illustrates the absorption spectra in aqueous solution of some of the representative compounds of Formula **I**.

[0128] Absorption spectra of the QAS-dyes from Examples 1-6 are shown in Figure 7. The bi-QAS substituted dyes showed greater bathochromicity (*i.e.*, shift to longer wavelengths) compared to the mono-QAS substituted dyes. Furthermore, with an increase in the alkyl chain length in the QAS, mono-QAS substituted dyes had the same λ_{max} at 379 nm while bi-QAS substituted dyes showed a bathochromic shift. Without being bound by any particular theory, it is believed that this bathochromic shift is related to the increased steric hindrance caused by the longer alkyl chains in the bi-QAS substituted dyes. As shown in Figure 8, three types of hydrogen bonding can occur with these compounds: intramolecular hydrogen bonding, intermolecular hydrogen bonding, and hydrogen bonding with water molecules in the aqueous solution. It is believed that intramolecular hydrogen bonding can lead to a bathochromic shift through a combination of two effects: (a) enhancing the electron-donating ability of the amide group and the electron-withdrawing ability of the carbonyl group; and (b) holding the groups in a planar conformation. *See,* for example, Gordon et al., *Organic chemistry in colour*, New York: Springer-Verlag Berlin Heidelberg; (1983). However, it is believed that the formation of the other two types of hydrogen bonding has no such effect. In the case of the bi-QAS substituted dyes, it is believed that with an increase in the alkyl chain length in the QAS, steric hindrance is increased, which can also increase the relative amount of intramolecular hydrogen bonding but decrease the proportion of the other two types of hydrogen bonding. Therefore, increasing QAS chain length resulted in greater bathochromicity for the bi-QAS substituted dyes. The steric hindrance effect of the alkyl chain was not obvious with mono-QAS substituted dyes.

[0129] In general, with an increase in the alkyl chain length in the QAS, all of the compounds showed a decrease in ε_{max}. Typically, ε_{max} is a widely-accepted measurement of tinctorial strength. However, assessing the tinctorial strength of dyes is quite difficult and, in some cases, controversial results are obtained. *Id.* For example, an empirical rule states that for a given series of dyes, the tinctorial strength increases as the dyes become more

bathochromic, whereas molecular orbital theory predicts that the tinctorial strength of dyes should decrease as λ_{max} increases. However, as a general rule, steric hindrance always causes a reduction in tinctorial strength. *Id.*

Example 10

[0130] This example illustrates the simultaneous dyeing and antimicrobial finishing of acrylic fabrics using the compounds of the present invention.

Materials and Methods:

[0131] Sulfonate-containing acrylic fabrics, *e.g.*, spun Orlon 75 (#864), were purchased from Testfabrics Inc. The fabrics were scoured in a solution of 5 g/L nonionic surfactant (Triton X-100, EM Science) at 60°C for 30 minutes, then rinsed thoroughly in tap water and dried in the open air. Sodium sulfate (EM Science), sulfuric acid (EM Science), sodium acetate (EM Science), and acetic acid (99%, EM Science) were used as received.

[0132] The dyeing of acrylic fabrics follows a traditional exhaustion dyeing procedure (Munn, *The dyeing of synthetic-polymer and acetate fibres*, England: Dyers Company Publications Trust (1979)). Dye solutions were prepared with the QAS-dyes of the present invention, sodium sulfate (2 g/L), and Triton X-100 (0.05%). The pH of the dyeing bath was adjusted to 3 by buffer solutions containing sulfuric acid, sodium acetate, and acetic acid. The bath ratio was kept at 1:50. The Orlon fabrics were immersed into the dyeing bath at initial dyeing temperatures for a certain period of time, and then fixed at 100°C for another period of time to elevate the interactions between the fabrics and the QAS-dyes.

[0133] A Hitachi U-2000 UV-vis spectrophotometer was used to measure the UV-vis absorbance of the dye solutions before and after exhaustion. The concentration of the QAS-dyes was calculated based on a previously established absorbance-concentration relationship at the λ_{max} of the compound. Unfixed compound from the samples was extracted by hot water and also measured by the UV-vis spectrophotometer. The amount of QAS-dye fixed on the fabric (F, mMol/Kg) was calculated by Eq. (1):

$$F = (N_0\text{-}N_1\text{-}N_2)/W, \quad (1)$$

where N_0 (μMol) is the initial QAS-dye quantity before exhaustion, N_1 (μMol) is the residual QAS-dye amount after exhaustion, N_2 (μMol) is the amount of unfixed QAS-dye present in the extracted solution, and W (g) is the weight of untreated Orlon fabric.

[0134] The antimicrobial activities of the treated Orlon fabrics were evaluated against *Escherichia coli (E. coli,* Gram-negative*)* and *Staphylococcus aureus* (*S. aureus,* Gram-positive) according to AATCC test method 100-1999. In this method, disposable petri dishes containing fabric swatches weighing about 1 g were challenged with 1.0 ± 0.1 mL of bacteria inoculum. After a certain period of contact time, the challenged fabric swatches were transferred to 250 mL containers with 100 mL of sterilized water, and the resultant supernatant was diluted 10^1, 10^2, 10^3, and 10^4 times. Then, 100 μL of each dilution was placed onto nutrient agar and incubated at 37°C for 18 hours. The same procedure was applied to an untreated Orlon fabric swatch as a control. Finally, viable bacteria colonies on the agar plate were counted, and the amount of bacterial reduction was calculated using Eq. (2):

$$\text{Reduction percentage (\%)} = (A\text{-}B)/A \times 100\%, \qquad (2)$$

where A represents the number of bacterial colonies in the control, and B represents the number of bacterial colonies in the treated Orlon fabrics.

[0135] The surface resistivity of the treated fabrics was measured by a portable surface resistivity/resistance meter purchase from Monroe Electronics, Inc (Model 272A). The visual color yields of the dyed fabrics were measured by GretagMacbeth™ Color-Eye® 7000A spectrophotometer. The visual color yields of the fabrics were expressed by K/S values, which were derived from the reflectance measurement. The treated fabric was washed in a Launder-Ometer® according to AATCC Test Method 61-2001 to evaluate the wash durability of the treated fabrics. In this method, one cycle of a Launder-Ometer wash is equivalent to five machine washes using a home laundry machine.

Results and Discussion:

[0136] **Effect of dyeing time:** The effect of dyeing time on the dyeing behavior of the QAS-dyes of the present invention was investigated. As shown in Figure 9, all the mono-QAS substituted dyes (*i.e.,* m-4, m-8, and m-12) showed higher fixation values than the corresponding bi-QAS substituted dyes (*i.e.,* bi-4, bi-8, and bi-12). For example, the fixation of m-4 was higher than that of bi-4, and the fixation of m-8 was higher than that of bi-8. Also, for both mono-QAS substituted and bi-QAS substituted dyes, the fabrics exhibited increased fixation with an increase in the alkyl chain length in the QAS.

[0137] Without being bound to any particular theory, it is believed that these results can be explained by the thermodynamic characteristics of the dyeing process. It is well established that the dyeing of most fibers is a thermodynamically reversible process. Therefore, it is permissible to apply thermodynamic functions to the dye-fiber systems (Bird *et al.*, *The theory of coloration of textiles*, London: Dyers Company Publications Trust (1975)). In a dye-fiber system, dyes are distributed in both the fiber and the dyebath. If A_f represents the activity of the dye in the fiber and A_d represents the activity of the dye in the dyebath, then the chemical potential of the dye in the fibers (μ_f) and in the dyebath (μ_d) can be expressed by the following equations, Eq. (3) and Eq. (4):

$$\mu_f = \mu_f^\circ + RT\ln A_f \quad (3)$$

$$\mu_d = \mu_d^\circ + RT\ln A_d, \quad (4)$$

where μ_f° and μ_d° are the chemical potentials when the activity is unity, *i.e.,* when the substance is in its standard state.

At equilibrium, μ_f equals μ_d, and therefore:

$$\mu_f^\circ + RT\ln A_f = \mu_d^\circ + RT\ln A_d, \text{ and}$$

$$-\Delta\mu^\circ = -(\mu_f^\circ - \mu_d^\circ) = RT\ln(A_f/A_d). \quad (5)$$

[0138] In the dyeing process, $-\Delta\mu^\circ$ is referred to as the standard affinity and is a measure of the tendency of the dye to move from its standard state in the dyebath onto the fiber. If Van der Waals interactions between dyes and fabrics are stronger, as the value A_f increases, the value of $-\Delta\mu^\circ$ also increases. In other words, with the increase of Van der Waals interactions between dyes and fabrics, more dyes may tend to move from the dyebath to the fiber, leading to higher fixation and/or dyeing results.

[0139] The bi-QAS substituted dyes contain two positively charged nitrogen atoms in each structure. As such, compared to the mono-QAS substituted dyes, they are more favorable to stay in the dyebath. Both $-\Delta\mu^\circ$ and the amount of fixation are lower for the bi-QAS substituted dyes. For both types of QAS-dyes, an increase in the alkyl chain length in the QAS results in an increase in hydrophobicity, indicating that the QAS-dyes can become less favorable to stay in the dyebath. On the other hand, with an increase in the alkyl chain length in the QAS, the Van der Waals interactions between the fabric and the QAS-dye increase. Thus, longer alkyl chains in the QAS result in increased $-\Delta\mu^\circ$ and higher fixation for both mono- and bi-QAS substituted dyes.

[0140] Figure 9 shows that the mono-QAS substituted dyes approached equilibrium after 120 minutes, while the bi-QAS substituted dyes needed as long as 300 minutes to level off. Without being bound to any particular theory, it is believed that these results can be explained by the thermodynamic characteristics of the dyeing process. Compared to the bi-QAS substituted dyes, the mono-QAS substituted dyes are less favorable to stay in the dyebath. As such, they are more favorable to the fiber. Because the A_f and $-\Delta\mu^o$ values can be higher for the mono-QAS substituted dyes, more dye can be driven to the fiber to occupy the dye sites, and an equilibrium is achieved faster.

[0141] The fiber saturation value of Orlon 75 is 2.5% (Munn, *The dyeing of synthetic-polymer and acetate fibres*, England: Dyers Company Publications Trust (1979)), which means that 1 g of Orlon can bind 2.5% of a pure basic dyestuff called malachite green crystals (MW=400 g/mol) if all the dye sites are occupied by the dye. Based on this definition, 1 g of Orlon can bind 0.025 g malachite green crystals. In other words, theoretically, 1 g of Orlon can bind 0.0000625 Mol of the dye, or 1 kg of Orlon contains 62.5 mMol of anionic dye sites.

[0142] The fixation of m-12 is around 60 mMol/kg, very close to the theoretical value, and the fixation of bi-12 is around 30 mMol/kg, half of the calculated value. Without being bound to any particular theory, it is believed that this can be caused by the fact that each mono-QAS substituted dye occupies one dye site within the fabric during fixation, while each bi-QAS substituted dye occupies two dye sites. However, dyes with shorter QAS alkyl chains, such as m-4, m-8, bi-4, and bi-8, showed lower fixation levels compared to the calculated value. Weaker Van der Waals interactions present between the QAS-dyes and the fabrics, which makes A_f smaller and $-\Delta\mu^o$ lower, can account for the lower fixation levels. Therefore, compared to m-12 or bi-12, these QAS-dyes are more favorable to the dyebath, and as such, do not fully occupy all of the dye sites on the fabrics.

[0143] Generally, the size of the dye can also play an important role in the dyeing process. Smaller dyes can diffuse faster into the fabric, while larger ones can diffuse more slowly. However, a calculation of the sizes of the QAS-dyes of the present invention indicates that all them have maximum diameters within 1~ 2.5 nm, as shown in Table 2. Since these QAS-dyes are small and their size differences are not significant, they have similar diffusion properties and the size of the compounds has little or no influence on the level of fixation.

Table 2. Molecular sizes of the QAS-dyes calculated by "HyperChem" software (edition 7.0) using semi-empirical, AM1, and geometry optimization.

Dyes	m-4	m-8	m-12	bi-4	bi-8	bi-12
Maximum diameter (nm)	1.19	1.25	1.35	1.80	2.16	2.20

[0144] Figure 9 also shows that QAS-dye saturation is achieved at about 120 minutes for the mono-QAS substituted dyes and at about 300 minutes for the bi-QAS substituted dyes.

[0145] **Effect of dye concentration:** The effect of dye concentration on the dyeing behavior of the QAS-dyes of the present invention was also investigated. As shown in Figure 10, all of the mono-QAS substituted dyes showed higher fixation values than the corresponding bi-QAS substituted dyes. In addition, the fabrics exhibited an increased level of fixation with an increase in the alkyl chain length in the QAS for both mono- and bi-QAS substituted dyes.

[0146] Although the results shown in Figure 10 are very similar to those shown in Figure 9, the fixed amount of dye for each QAS-dye was lower in Figure 10. Without being bound to any particular theory, it is believed that the shorter dyeing and fixation period (60 minutes total) can account for the lower level of fixation.

[0147] The number of cations present in the QAS-dyes of the present invnetion can also contribute to different dye fixation values. As mentioned earlier, the bi-QAS substituted dyes occupy twice the amount of dye sites within the fabrics compared to the mono-QAS substituted dyes. Therefore, theoretically, the value of fixed bi-QAS substituted dyes should be only half the amount of the mono-QAS substituted dyes if the dye sites are constant and fully occupied. However, the data from Figures 9 and 10 indicate that the dyes sites are not fully occupied. As such, the number of cations present in the QAS-dyes is not a major factor in determining the amount of fixed QAS-dye.

[0148] **Effect of dyeing temperature:** The effect of temperature on the dyeing behavior of the QAS-dyes of the present invention was also investigated. Figure 11 shows that, below 80°C, only a small amount of QAS-dyes was fixed onto the Orlon fabric. However, when the temperature was increased from 80°C to 90°C, an increase of about two-fold was observed for all compounds. Furthermore, when the temperature was increased

from 90°C to 100°C, an increase of about three-fold was observed for the mono-QAS substituted dyes, and about two-fold for the bi-QAS substituted dyes.

[0149] Without being bound to any particular theory, it is believed that the glass transition temperature (Tg) of the fabrics can account for these results. It has been reported that in acrylic dyeing, only a few dye molecules can enter the polymers below Tg due to their highly compact structure (Burkinshaw, *Chemical principles of synthetic fibre dyeing*, Glasgow: Blackie Academic & Professional, Chapman & Hall (1995); Munn, *The dyeing of synthetic-polymer and acetate fibres*, England: Dyers Company Publications Trust (1979)). Tg denotes the temperature at which polymers change from a glassy state to a rubbery one. At or about the Tg of the fiber, the movement of the polymer segments begins. With a further increase in temperature, segment mobility becomes more pronounced, and the free volume can be increased exponentially within the polymers, allowing dyes greater accessibility to the polymers.

[0150] The study by Munn showed that unmodified polyacrylonitrile fibers had a very high Tg due to its highly compact structure, but the copolymerization of acrylonitrile with other co-monomers brought about a decrease in Tg. Depending on the type of co-monomer used and the amount of co-monomer added, Tg of the acrylic fibers varied from 60°C to 80°C. Higher than these temperatures, the free volume of acrylics can increase dramatically, and the accessibility of dye sites and the rate of dye diffusion can also increase correspondingly. Therefore, for the data shown in Figure 11, while the levels of dye fixation began to increase around 80°C, further increases in temperature led to a dramatic increase in dye fixation levels.

[0151] **FTIR analysis:** To confirm the incorporation of the QAS-dyes of the present invention into the fabrics, the treated Orlon fabrics were analyzed by FTIR. Figure 12 shows a typical example of the FTIR spectra in the range of 1000-2000 cm^{-1} for m-4. In the spectrum of untreated Orlon (A), a strong adsorption band centered at 1732 cm^{-1} was observed, corresponding to the carbonyl groups of the acrylate co-monomers. The weak peak at 1630 cm^{-1} is most likely caused by the impurities of the fibers (Sun *et al.*, *J. Appl. Polym. Sci.*, 65:959 (1997)). In the spectrum of the m-4 treated fabric (B), although several shoulders appeared, they overlapped with the 1630 cm^{-1} band. After subtracting (A) from (B), their difference spectrum was obtained (C), which represents the sum of the m-4 contribution to the dyed fabrics as well as any changes due to the interactions between the

QAS-dyes and the fabrics. It can be seen clearly in spectrum (C) that the 1630 cm^{-1} band disappears, and two new peaks centered at 1706 cm^{-1} and 1673 cm^{-1} appear. The peak at 1706 cm^{-1} can be attributed to the amide carbonyl group in the QAS-dye, and the band around 1673 cm^{-1} may be caused the carbonyl group present in the anthraquinone ring of the QAS-dye. These assumptions are further confirmed by the spectrum of pure m-4, as shown in (D).

[0152] The spectrum of Orlon fabrics treated with bi-QAS substituted dyes exhibits a slightly different FTIR spectrum pattern than with mono-QAS substituted dyes such as m-4. For example, Figure 13 shows the spectrum of Orlon treated with bi-12 (b). It can be seen that around 1630 cm^{-1}, the shoulders become less obvious. However, after subtracting (A) from (B), their difference spectrum (C) also exhibited a new peak at 1718 cm^{-1}, corresponding to the amide carbonyl group in the QAS-dye.

[0153] Figure 14 summarizes the FTIR spectra of Orlon fabrics treated by both mono- and bi-QAS substituted dyes. It can be seen that all of the fabrics treated with the mono-QAS substituted dyes show very similar results, as do the fabrics treated with the bi-QAS substituted dyes. Therefore, it can be concluded that all of the synthesized antimicrobial cationic dyes (*i.e.,* QAS-dyes) of the present invention can be incorporated into Orlon fabrics by following the traditional cationic dyeing process.

[0154] **Antimicrobial Properties:** The antimicrobial efficacy of the Orlon fabrics treated with the QAS-dyes of the present invention was studied. Table 3 shows the effect of different concentrations of bacteria and contact time. It can be seen that an increase of bacterial concentration caused a decrease of fabric antimicrobial activity at each contact time. When the *E. coli* concentration was lower than 10^7 CFU/mL, the treated fabrics showed the highest antimicrobial efficacy after 6 hours of contact. With a further increase or decrease in contact time, the antimicrobial activity decreased. However, when the bacterial concentration was higher than 10^7 CFU/mL, the fabric showed 86.7% of inactivation at 3 hours of contact. Longer contact times exhibited no antimicrobial activity.

Table 3. The effect of bacterial concentrations and contact time.

E. coli concentration (CFU/mL)	Contact time (hrs)			
	3	6	9	12
10^5~10^6	93.3%	99.9%	93.3%	66.7%
10^6~10^7	92.5%	95.8%	83.3%	50%

10^7~10^8	86.7%	0%	0%	0%

All fabrics were treated with 1 mMol/L of bi-12 at pH 3. Dyeing: 100°C for 50 min.; fixation: 100°C for 10 min. Bath ratio: 1:50.

[0155] Without being bound to any particular theory, it is believed that these results can be explained by the antimicrobial mechanism of the QAS-dyes. It has been reported that the quaternary ammonium salt (QAS), the active antimicrobial component of the QAS-dye, kills microorganisms by disturbing their cytoplasmic membranes (Latlief *et al.*, *J. Pediatrics*, 39:730 (1951)). During this process, a competition may exist between the death and the growth of bacteria. When the *E. coli* concentration is lower than 10^7 CFU/mL, in the beginning of the contact, the dyes may be able to kill the bacteria efficiently. When the contact time increases to 6 hours, the antimicrobial efficacy also increases due to more efficient contact. However, a further increase in contact time may use up all of the available QAS-dye, resulting in the favorable the growth of bacteria and decreased antimicrobial efficacy. When the bacterial concentration is higher than 10^7 CFU/mL, the QAS-dye concentration is relatively low compared to that of the bacteria, so even in the beginning, low antimicrobial efficacy is observed. All of the available QAS-dye may be used up quickly in this case, and as a result, a further increase of contact time does not cause bacterial reduction.

[0156] The treated Orlon fabrics were further challenged against *E. coli* and *S. aureus*. As shown in Table 4, prior to washing, all of the treated fabrics provide efficient antimicrobial activity, but to different degrees depending on the QAS-dye. Generally, for both mono- and bi-QAS substituted dyes, an increase in the alkyl chain length in the QAS resulted in higher fabric antimicrobial efficacy. For example, the Orlon fabric treated by m-4 can kill 95.7% of *E. coli*, and the Orlon fabric treated by m-12 can kill 99.9%. In most cases, the fabrics treated by the bi-QAS substituted dyes exhibited higher antimicrobial efficiency compared to the dyes treated by the corresponding mono-QAS substituted dyes. For example, the fabric treated by bi-8 can kill 93.9% of *S. aureus,* and the fabric treated by m-8 can kill 92.4%. Also, all the treated fabrics show higher antimicrobial efficacy against *E. coli* than *S. aureus*.

Table 4. Antimicrobial efficacy of fabrics treated with compounds of the present invention.

		Orlon treated with:

Wash times	Bacteria	Orlon treated with:					
		m-4	m-8	m-12	bi-4	bi-8	bi-12
0 washes	*E. coli*	95.7%	98.6%	99.9%	97.1%	98.6%	99.9%
	S. aureus	86.4%	92.4%	99.9%	87.5%	93.9%	99.9%
5 washes	*E. coli*	44.0%	44.0%	81.3%	37.5%	50.0%	99.3%
	S. aureus	50.0%	37.5%	75.0%	36.4%	50.0%	81.8%
10 washes	*E. coli*	0%	0%	0%	0%	46.7%	60.0%
	S. aureus	0%	0%	0%	0%	37.5%	45.5%
20 washes	*E. coli*	0%	0%	0%	0%	0%	0%
	S. aureus	0%	0%	0%	0%	0%	0%

All fabrics were treated by 1 mMol/L of the compound at pH 3. Dyeing: 100°C for 50 min.; fixation: 100°C for 10 min. Bath ratio: 1:50. *E. coli* or *S. aureus* concentration: 10^5~10^6 CFU/mL; contact time: 6 hrs.

[0157] As mentioned earlier, the active antimicrobial component of the QAS-dye, the QAS, kills bacteria by disturbing their cytoplasmic membranes. Shorter alkyl chains on the QAS (*e.g.*, less than 8 carbons) show weaker antimicrobial activities. Without being bound to any particular theory, it is believed that the higher antimicrobial activities of the fabrics treated with the bi-QAS substituted dyes are caused by the higher QAS content in the dyes, and the higher antimicrobial efficacy against *E. coli* is related to the fact that *E. coli* shows less resistance to mechanical rupture compared to *S. aureus* (Hugo, *J. Appl. Bact.*, 30:17 (1967)).

[0158] Table 4 shows that the wash durability of the treated fabrics was low. For example, after 5 washes, the fabric treated by m-12 killed 81.3% of *E. coli*; after 10 washes, the antimicrobial activities disappeared except for bi-8 and bi-12. Fabrics treated with bi-12 achieved the best results: after 5 washes, the fabric killed 99.3% of *E. coli*; after 10 washes, the antimicrobial efficiency was 60.0%. Without being bound to any particular theory, it is believed that the low washing durability of the treated Orlon fabrics is caused by the loss of the QAS-dyes during washing. To confirm this assumption, the surface resistivity (*i.e.*, anti-static property) of these fabrics was measured. As shown in Figure 15, all of the dyed fabrics had lower surface resistivity (*i.e.*, less static) than untreated Orlon, indicating that the electric conductivity of the dyed fabrics was higher due to the incorporation of the dyes. As such, the

QAS-dyes of the present invention are also suitable for use as anti-static agents. With an increase in the number of washes, the surface resistivity increased (*i.e.*, more static), indicating a decrease in the conductivity of the fabrics. Without being bound to any particular theory, it is believed that this decrease is caused by the loss of some of the dye.

[0159] To further confirm the loss of QAS-dyes during washing, the K/S values of the samples were also measured. As shown in Table 5, the K/S values also showed a slight decrease after washing; however, the change was not significant, indicating that the visual effects are not influenced significantly.

Table 5. The visual color yields of the fabrics (K/S values).

Wash times		Orlon treated by					
		m-4	m-8	m-12	bi-4	bi-8	bi-12
0 washes	K/S	4.80	6.96	6.00	1.52	2.32	1.60
	λ_{max} (nm)	390	390	390	450	450	450
5 washes	K/S	4.72	6.88	5.80	1.52	2.20	1.52
	λ_{max} (nm)	390	390	390	450	450	450
10 washes	K/S	4.72	6.44	5.80	1.44	2.20	1.52
	λ_{max} (nm)	390	390	390	450	450	450
20 washes	K/S	4.72	6.32	5.78	1.44	2.20	1.52
	λ_{max} (nm)	390	390	390	450	450	450

[0160] Due to the hydrophobic nature of Orlon fabrics, there may not be sufficient contact between the fabrics and the bacterial or detergent solutions during the experiments. Without being bound to any particular theory, it is believed that the fixed dyes may be divided into water-accessible and water-inaccessible fractions when the temperature is below the Tg of the fabrics. The water-accessible dyes mainly locate on the surface of the fabrics. In the antimicrobial test, it is the water-accessible dyes that contribute to the antimicrobial efficacy of the treated Orlon, since only they can come into contact with the bacteria and thus kill the bacteria. During washing, it is also these water-accessible dyes that are washed away, since they can come into contact with the detergent solutions. After washing, the antimicrobial activity of the treated fabrics dropped significantly, due to the loss of water-accessible dyes.

[0161] The surface resistivity indicates the amount of dye bound to the surface of the fabrics. Without being bound to any particular theory, it is believed that most of these surface dyes are water-accessible and are lost during washing. Therefore, the surface resistivity of the fabrics was very different before washing compared to after washing. However, K/S measures the shade depth of the fabrics (Yang *et al.*, *AATCC Review*, 3:29 (2003)). As both water-accessible dyes and water-inaccessible dyes inside the fabrics contribute to the shade depth, the total visual effect is not significantly affected by the loss of the water-accessible dyes.

[0162] After dyeing, all of the dyes showed a different λ_{max} in the fabrics compared to that in aqueous solutions (Ma *et al.*, *Dyes and Pigments*, 58:27 (2003)). For example, the Orlon fabric treated with m-4 exhibited a λ_{max} at 390 nm, while the aqueous solution of m-4 had a λ_{max} at 379 nm. As mentioned earlier, K/S measures the shade depth of the fabric and is influenced by dye concentration, the physical state of the dye, as well as the surface structure of the fabric. The physical state of the dye in the fabric is different from that in the aqueous solution, and as a result, a bathochromic shift of the dye is observed in the Orlon fabric. In addition, the fabric structure can influence the λ_{max}. Table 5 also shows that none of the treated fabrics had a change in λ_{max} after washing, indicating that the fixed dyes were stable and decomposition and/or other structural changes did not occur during washing.

Example 11

[0163] This example illustrates the thermal and hydrolytic stability of compounds of the present invention.

Materials and Methods:

[0164] **Thermal stability analysis:** Thermal analyses of the QAS-dyes shown in Figure 2B were performed using a differential scanning calorimeter (DSC) (Shimadzu DSC-50) and a thermal gravimetric analyzer (TGA) (Shimadzu TGA-50). The dye samples were heated at 10°C/min. and nitrogen gas was chosen as the atmosphere.

[0165] **Hydrolytic stability analysis:** The dyes were dissolved in aqueous solutions at a concentration of 0.4-1 mMol/L, and the solutions were adjusted to various pH values by using sulfuric acid, acetic acid, sodium acetate, sodium bicarbonate, and/or sodium carbonate. The solutions were heated to the required temperatures. At different time intervals, solution samples were taken and measured by a HITACHI U-2000 spectrophotometer to obtain the

UV-vis adsorption spectra. The results were compared with the spectra of original dye solutions to determine the stability of the dyes.

[0166] After hydrolysis, the precipitates formed in the dye solutions were filtered and thoroughly washed with deionized water. The resultant precipitates were recrystallized using acetone for NMR analysis. NMR spectra were recorded on a Varian Inova 400 spectrometer. The residual filtrate was extracted by chloroform, and the aqueous part was dried under vacuum at room temperature and analyzed by NMR.

Results and Discussion:

[0167] **Thermal stability:** As shown in Figure 16, there were no obvious changes observed up to 190°C in the DSC spectra of the mono-QAS substituted dyes (m-4, m-8, and m-12), indicating that the dyes are stable below this temperature. Above 90°C, all dyes exhibited a sharp endothermic peak centered around 205-219°C. Thereafter, a wide exothermic peak in the range of 320-440°C was detected. As shown in Figure 17, TGA analysis of the same samples indicated that these peaks corresponded to the decomposition of the dyes. This thermal decomposition involved two steps: the first step occurred in the temperature range of 200°C to 240°C, representing a weight loss of more than 25%; and the second step ended at 400°C, leading to carbonization of the products. At temperatures higher than 400°C, no further weight loss could be detected. The total weight losses were more than 70%.

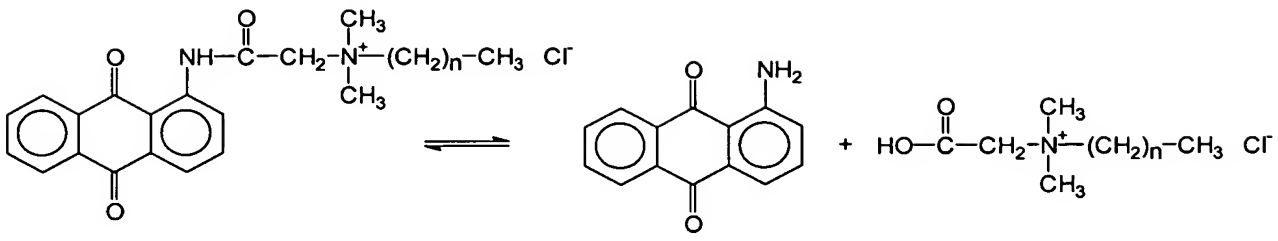
[0168] Generally, anthraquinone structures are thermally stable (Gordon *et al.*, *Organic chemistry in colour*, Berlin: Springer-Verlag (1983)). Thus, the decomposition of the dyes may be caused by the attached quaternary ammonium salt group. The thermal stabilities of quaternary ammonium salts have been investigated elsewhere, and the first stage of the thermal decomposition of a QAS is a dealkylation reaction, caused by a nucleophilic substitution reaction of the halide ion (X^-) at the α carbon center (Fenton *et al.*, *J. Chem. Soc.*, 989 (1933)). The whole process can be regarded as the reverse of quaternization of tertiary amines (Blazejowski *et al.*, *Thermochimica Acta*, 92:811 (1985); Rodd, *Chemistry of carbon compounds*, Vol. 1, part A, Amsterdam: Elsevier (1951)). Typically, the attack of X^- on the most positive carbon atom is a thermodynamically favored reaction (Blazejowski *et al.*, *id*). However, in thermal degradations, because of the high reaction temperatures, the selectivity of the substitution can be significantly reduced, and various substituted products are obtained. The emission of these newly formed alkyl chloride or amine compounds accounts for the

initial weight loss of the samples at 200°C. The exothermic peak of the second step of the weight loss in the TGA curves is most likely attributed to the decomposition of the anthraquinone dye structures. Again, because of the same decomposition mechanisms, the DSC and TGA curves of the samples have very similar patterns in this range.

[0169] Similar phenomena can be observed in the thermal analysis of bi-QAS substituted dyes. All of the results indicate that the synthesized dyes are stable under 190°C, which is sufficient for the one-step dyeing and finishing process of the present invention.

[0170] **Hydrolysis of dyes:** The hydrolytic stability of the mono-QAS substituted dyes was examined with a UV-visible spectrometer. For example, Figure 18 shows the absorption spectra of an m-4 dye solution at 100°C and at pH 5 at different times. The m-4 dye solution (0.4 mMol/L) was stable for about six hours, evidenced by the almost unchanged visible spectra. After 8 hours, however, the absorbance of the dye solution decreased dramatically. Accompanying the decrease in absorbance, a red precipitate was also observed in the solution. ^{1}H NMR analysis of the precipitate indicated that 1-aminoanthraquinone was produced as one of the hydrolytic products of m-4 (Figure 19). Theoretically, aromatic amines absorb from 3.0 to 5.0 ppm (Silverstein *et al.*, *Spectrometric identification of organic compounds*, New York: John Wiley & Sons (1998)). However, because hydrogen bonding can occur between the amine and the trace water present in the sample, the peak of the amine protons may be shifted and overlap with other peaks. Therefore, in Figure 19, proton H_h cannot be detected. In fact, in the ^{1}H NMR standard spectrum of 1-aminoanthraquinone, the amine protons appear at 7.98 ppm, overlapping with protons H_e and H_f (Sadtler spectra, 300 MHz proton nuclear magnetic resonance standards, 1793 HB).

[0171] When the filtrate solution of the hydrolyzed m-4 dye was dried under vacuum, a solid compound was obtained. Both ^{1}H NMR (Figure 20) and ^{13}C NMR (Figure 21) spectra of this compound were measured. Based on this analysis, the compound was confirmed to be carboxylmethyl-butyl-dimethyl ammonium chloride (CBDAC). The confirmation of both 1-amino-anthroquinon and CBDAC indicated that the hydrolysis of m-4 was caused by the cleavage of the amide linkage. Similar results were obtained in the hydrolytic analysis of both m-8 and m-12. The hydrolysis reaction of the mono-QAS substituted dyes can be expressed by Eq. (6):



Mono-substituted dyes

n=3: m-4
n=7: m-8
n=11: m-12

1-amino-anthraquinone

Alkylbetaine

n=3: butylbetaine
n=7: octylbetaine
n=11: dodecylbetaine

(6)

[0172] The hydrolytic stability of one of the bi-QAS substituted dyes, bi-4, was conducted at pH 5 and at 100°C (0.5 mMol/L), and a purple precipitate was observed as one of the hydrolytic products. ^{1}H NMR analysis confirmed that 1,4-diaminoanthraquinone was the compound present in the precipitate (Figure 22). Similarly, CBDAC was also found in the filtrate solution of hydrolyzed bi-4. Both bi-8 and bi-12 also exhibited the formation of 1,4-diaminoanthraquinone and the corresponding carboxylalkyl ammonium chlorides, indicating that bi-substituted dyes also undergo hydrolysis through the cleavage of amide linkages.

[0173] **Effect of pH:** The amide linkage between anthraquinone and a quaternary ammonium salt group is vulnerable to hydrolysis. Different pH conditions may affect the hydrolysis as well. Figure 23 shows the period of stability for three different mono-QAS substituted dye solutions at different pH values. All of the dyes tested exhibited the highest stability at pH 3. As such, rather than being stable at the neutral conditions, mono-QAS substituted dyes surprisingly showed the highest stability at an acidic pH. Without being bound to any particular theory, this result is associated with the unique structures of the QAS-dyes of the present invention, as these dyes possess both hydrophobic and hydrophilic features, similar to surfactants.

[0174] With an increase in alkyl chain length, the hydrophobicity of the dye is improved. The surfactant feature of these dyes indicates that the dyes may have properties similar to surfactants in aqueous solutions. For example, the dyes can aggregate in water to form micelles by placing the hydrophilic segment at the outer layer and pushing the hydrophobic alkyl chain into the inner layer. Since the hydrophilic moiety contains a positively charged nitrogen atom, the hydrophilic sections of the aggregates and the outer layer of the micelles possess positive charges. Thus, the aggregates and micelles tend to

attract negatively charged species but repel positive ones in the solution. In other words, hydroxide ions (OH^-) can be favorably attracted to the aggregates or micelles but protons (H^+) are repelled from them. The close interactions between OH^- and the QAS-dyes would lead to hydrolysis, which explains the observed lower dye stability at higher pH values. With a decrease in pH, the concentration of OH^- decreases, while that of H^+ increases. However, under weakly acidic conditions, H^+ may not be fully accessible to the amide bonds due to the repulsion between the positively charged hydrophilic end and H^+, so hydrolysis may not occur and the stability of the dyes maintains until the pH reaches 3. With a further decrease in pH, the concentration of H^+ is further increased. At the same time, the concentration gradient may also increase around the aggregates and micelles, and a strong driving force can be formed, surpassing the repulsive interactions. Therefore, H^+ may be able to come close to the aggregates or micelles, the hydrolysis of the amide groups begins to follow the "normal" acid-catalyzed hydrolysis pathway, and the stability of the dyes gradually decreases accordingly.

[0175] The attraction/repulsion-induced hydrolysis of amide linkages is not an unusual phenomenon. In studying the hydrolytic stability of acethydrazide and acetamide, Edward *et al.* (*J. Chem. Soc.*, 2520 (1955)) reported that the former was hydrolyzed more slowly than the amide in weak acid because the positive charge of the protonated acethydrazide repelled hydrogen ions. In strong acid, however, this effect operated less strongly and the hydrolysis of acethydrazide became fast. Similar results were also reported in Lindegren *et al.*, *Amer. Chem. Soc.*, 71:1504 (1949); and Butterworth *et al.*, *Biochem. J.*, 53:30 (1953).

[0176] **Effect of alkyl chain length:** Different mono-QAS substituted dyes showed different stabilities under various pH conditions (*see,* Figure 23). For example, under acidic conditions, m-4 was more stable than m-8, which in turn was more stable than m-12. As mentioned earlier, the hydrolysis of the dyes occurred due to the cleavage of the amide linkages. The hydrolysis products were 1-aminoanthraquinone and the corresponding carboxyalkyl ammonium chlorides (*see,* Eq. (6)). Carboxyalkyl ammonium chlorides belong to a type of amphoteric surfactants called alkylbetaine (Domingo, *Amphoteric surfactants* (2^{nd} edition), Vol. 59, Edited by Lomax, New York: Marcel Dekker, Inc. (1996)). The solubility of alkylbetaines in water was highly dependent on the number of carbon atoms. Typicaly, the higher the alkyl chain length in betaines, the lower the solubility. For example, ethanesulfobetaine with a hexyl alkyl chain has a solubility of 655.0 g/L at 30°C, while the

solubility of the decyl homologue drops to 2.2 g/L, and that of the docosyl homologue was less than 0.1 g/L (Barnhurst, *J. Org. Chem.*, 26:4520 (1961)).

[0177] Without being bound to any particular theory, it is believed that the different solubilities of alkylbetaines may explain the different stabilities of the three mono-substituted dyes. In the case of m-8, the hydrolyzed product octylbetaine is less soluble in water compared to m-4 (butylbetaine), so it may precipitate out, leading to a lower concentration in the hydrolysis solution, and thus drive the hydrolysis equilibrium to the right (*see,* Eq. (6)). As a result, compared to m-4, a lower stability was observed for m-8. The hydrolysis of m-12 produces dodecylbetaine, which is even less soluble than octylbetaine, indicating that the concentration of dodecylbetaine is even lower in the solution and the equilibrium is shifted further to the right. As such, m-12 had the lowest stability. However, when the pH was higher than 7, all of the alkylbetaines can become deprotonated and the solubilities may be increased compared to the protonated forms. Therefore, the hydrolysis equilibriums of three dyes may not be affected as much as in acidic conditions, such that all of the dyes show similar stabilities at pH values higher than 7 (*see,* Figure 23).

[0178] The above explanation is supported by the observation of an opaque solution the formed when the pH was adjusted lower than 3, particularly in the hydrolysis of m-8 and m-12. The opaque solutions were caused by the low solubilities of octylbetaine and dodecylbetaine. In acidic conditions, they mostly exist in the protonated form that has relatively low solubility in water. In basic conditions, however, the deprotonated form becomes predominant (*see,* Eq. (6)). The relatively high solubility of the deprotonated alkylbetaines may decrease oily droplet formation. In the case of butylbetaine, due to its high solubility in both protonated and deprotonated forms, no opaqueness was observed in the hydrolysis of m-4.

[0179] The effect of pH on the hydrolysis of bi-QAS substituted dyes was also investigated. As shown in Figure 24, bi-QAS substituted dyes exhibited a similar stability trend with respect to pH as mono-QAS substituted dyes, although the bi-QAS substituted dyes had a lower overall stability. Without being bound to any particular theory, it is believed that this may be due to the fact that the bi-QAS substituted dyes have two amide linkages in each compound, making them more susceptible to acid or base attack.

[0180] All of the above-mentioned results indicate that the QAS-dyes of the present invention are stable within a pH range of from about 1 to about 4 at 100°C, with pH 3

providing the most optimal stability results. In textile (*e.g.*, acrylic) dyeing and finishing applications, the dyes may be exposed to both acidic conditions at high temperatures. As such, the dyes of the present invention are suitable for use in these applications, as they can withstand the conditions encountered therein.

[0181] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and scope of the appended claims. All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entirety for all purposes.